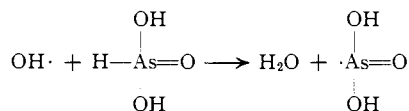Arsenic(III) is not easily oxidized by one-electron oxidants without the addition of catalysts but is readily oxidized by two-electron transfer. Waters[26] suggests that a one-electron oxidation of arsenic(III) can occur only when the oxidant is capable of withdrawing a hydrogen atom from the favored tautomer; e.g.

$$OH\cdot\ +\ H\!-\!\overset{\displaystyle OH}{\underset{\displaystyle OH}{As}}\!=\!O\ \longrightarrow\ H_2O\ +\ \cdot\overset{\displaystyle OH}{\underset{\displaystyle OH}{As}}\!=\!O$$

The sulfate free radical can also be considered as a hydrogen-extracting radical, producing HSO_4^- instead of

(26) W. A. Waters, *Discussions Faraday Soc.*, **29**, 170 (1960).

the formulated $SO_4{}^{2-}$. This proposed structure of As(IV) could also explain why the ion pair complex $FeOH^{2+}$ reacts faster with As(IV) than the Fe^{3+} does. The former reaction will be the direct transfer of a hydroxyl

$$FeOH^{2+}\ +\ AsO(OH)_2\ \longrightarrow\ Fe^{2+}\ +\ AsO(OH)_3$$
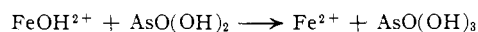
while the latter will involve electron transfer followed by the addition of hydroxyl ion

$$Fe^{3+}\ +\ \cdot AsO(OH)_2\ \longrightarrow\ Fe^{2+}\ +\ {}^+AsO(OH)_2\ \overset{OH^-}{\longrightarrow}\ AsO(OH)_3$$
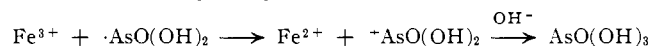
In conclusion, it is mentioned that oxygen has a great effect on the iron–arsenic–persulfate system, which is discussed in a subsequent paper.

[Contribution from the Department of Chemistry, University of California, Riverside, Calif.]

Properties and Infrared Spectra of Ethylenediaminetetraacetic Acid Complexes. V. Bonding and Structure of Several Metal Chelates in Solution

By Donald T. Sawyer and James E. Tackett

The ethylenediaminetetraacetic acid complexes of the alkaline earth ions, cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), manganese(II), lead(II), bismuth(III), cerium(III), aluminum(III), iron(III), chromium(III), thorium(IV), and vanadium(IV) in aqueous solution have been studied by infrared spectroscopy using deuterium oxide as the solvent. The effect of solution acidity upon the spectra has been determined and from this stability constants have been estimated for several of the chelate systems. The shift in peak position and area for the carboxylate–carboxylic acid absorption band has been used to propose structures for the complexes in solution. The data indicate that there is some tendency for metal–nitrogen coordination in the alkaline earth–EDTA chelates, but that such bonding is present to a much greater extent with the complexes of the divalent transition metal ions. The structures proposed for the iron(III), aluminum(III), and chromium(III) complexes are more complex and involve hydroxide groups as well as the EDTA ligand.

Although there have been a number of previous infrared studies of the metal–ethylenediaminetetraacetic acid (EDTA) complexes, these have been restricted to the solid phase; a previous paper in this series summarizes the literature.[1] The major importance of metal chelates is their behavior in solution, and in the case of EDTA, in aqueous solutions. Absorption of infrared radiation by water and the limitations imposed by cell materials have restricted studies of aqueous solutions. However, by using deuterium oxide and barium fluoride cells, certain regions of the infrared spectra for metal–EDTA chelates may be investigated, particularly the carbonyl region.

The present study is concerned with the effect of solution pH upon the peak position and area for the carboxylate–carboxylic acid absorption band for a number of metal–EDTA complexes in aqueous solution. The metal ions considered include the alkaline earths, the divalent transition metals, lead(II), iron(III), aluminum(III), chromium(III), bismuth(III), cerium(III), thorium(IV), and vanadium(IV). On the basis of the spectral changes with pH and the conclusions made earlier with respect to the structure of the free ligand,[2a,b] structures are proposed for the various metal–EDTA complexes in solution.

Experimental

Equipment.—The infrared spectra were recorded with a Perkin–Elmer model 421 spectrophotometer equipped with a high resolution grating. Some preliminary spectra were recorded with a Perkin–Elmer model 221G. The aqueous solutions of the metal chelates were contained in barium fluoride cells with 0.025-mm. spacers. The low solubility of this material in water prevented significant attack by the solutions; barium fluoride trans-

(1) D. T. Sawyer and J. M. McKinnie, *J. Am. Chem. Soc.*, **82**, 4191 (1960).

(2) (a) D. T. Sawyer and J. E. Tackett, *ibid.*, **85**, 314 (1963); (b) K. Nakamoto, Y. Morimoto, and A. E. Martell, *ibid.*, **85**, 309 (1963).

mits radiation down to 800 cm.$^{-1}$. The pH of the solutions was measured with a line-operated Leeds and Northrup pH meter equipped with microelectrodes. With such electrodes the total solution volume could be as small as 0.5 ml. The meter was standardized with N.B.S. buffers.

Reagents.—Deuterium oxide (D_2O) was used for the preparation of all solutions to avoid the interfering absorption bands of the H_2O molecule in the carbonyl region. The material was obtained from the Bio-Rad Laboratories, Richmond, Calif., and had an assay of 99.9% D_2O. The disodium salt of EDTA (as the dihydrate from the J. T. Baker Co.) was used without further purification and had an assay of 99.9%. All other materials were reagent grade. The metal ions were introduced as the metal chloride or nitrate salts, with the exception of thorium(IV) perchlorate.

The metal–EDTA solutions were prepared by combining weighed portions of the disodium salt of EDTA (Na_2H_2Y) and the metal salt with D_2O to give an equimolar stock solution of ligand and metal ion. Concentrated NaOH or HCl was added to aliquot portions of the prepared metal–EDTA solution to give the desired pH. Because the major acidic species present in the solutions was the solvated deuterium ion, the indicated pH values on the pH meter had to be corrected to give true acidity by using the equation of Mikkelson and Nielson[3]

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

By measuring the peak areas for differing carboxylate groups, the relative number of such differing groups was determined. The peak areas were measured using the base-line technique and ascertaining the absorbance at the base and at the peak. By taking the peak width at the half-height (in terms of absorbance) and multiplying by the peak height the approximate concentration of a given absorbing species was determined.

Results

The spectral shifts as a function of solution acidity (pD) for the alkaline earth–EDTA chelates in solution are quite similar, especially for the carbonyl region. A representative example of the effect of solution pD upon the carboxylate absorption band is given in Fig. 1 for the barium–EDTA complex. At low values of pD two peaks are observed, one at 1720 cm.$^{-1}$

(3) K. Mikkelson and S. O. Nielson, *J. Phys. Chem.*, **64**, 632 (1960).
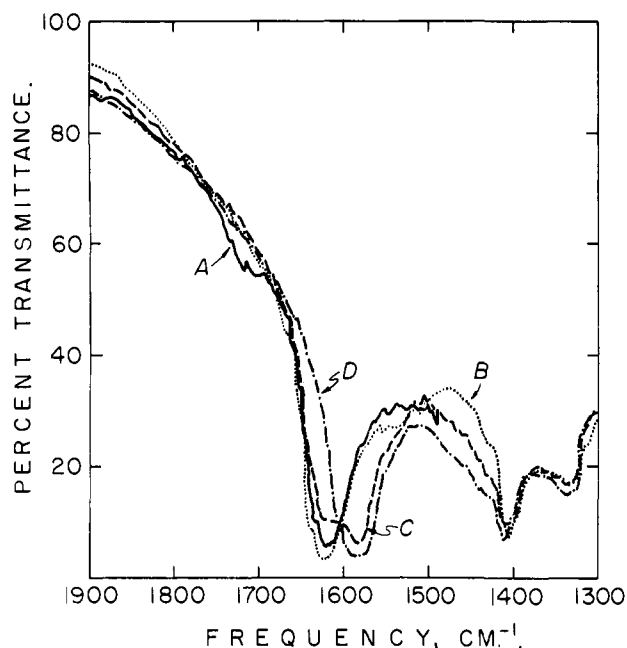
Fig. 1.—Spectra for 0.05 *F* barium–EDTA in D_2O as a function of solution acidity.

Curve	A	B	C	D
pD	2.9	4.9	5.9	11.6

Fig. 2.—Spectra for 0.05 *F* zinc–EDTA in D_2O as a function of solution acidity.

Curve	A	B	C
pD	0.9	2.2	11.4

Fig. 3.—Spectra for 0.05 *F* mercury(II)–EDTA in D_2O as a function of solution acidity.

Curve	A	B	C	D
pD	1.8	2.7	3.3	11.3

characteristic of carboxylic acids and one at 1620 cm.$^{-1}$. As the pD is increased the 1720 cm.$^{-1}$ peak disappears leaving only the 1620 cm.$^{-1}$ peak. With further increase of the pD a new band appears at 1580 cm.$^{-1}$ characteristic of an ionic carboxylate group and grows in area at the expense of the 1620 cm.$^{-1}$ peak. The peaks are approximately equal in area at pD 5.9 (curve C, Fig. 1); at basic values of pD only the 1580 cm.$^{-1}$ peak remains. The corrected values of pD for the conditions where the 1620 and 1580 cm.$^{-1}$ areas are equal for the alkaline earth–EDTA complexes are given in Table I, part A.

The EDTA chelates for the divalent ions of cobalt, nickel, copper, zinc, cadmium, and lead all give similar spectra in solution; Fig. 2 gives the spectra for zinc–EDTA as a function of pD and is representative of this group of metals. At low values of pD (curve A) two peaks are observed, one at 1720 cm.$^{-1}$ for the carboxylic acid group and one at 1600 cm.$^{-1}$. As the pD is increased the 1600 cm.$^{-1}$ peak grows at the expense of the 1720 cm.$^{-1}$ peak and it gradually decreases in frequency to 1590 cm.$^{-1}$. The corrected values of pD for the conditions where the area of the 1590–1600 cm.$^{-1}$ peak is at three-eighths its maximum value are given in Table I, part B.

The spectra for the mercury(II)–EDTA complex, Fig. 3, are somewhat unique in that three absorption peaks are observed at 1710, 1615, and 1595 cm.$^{-1}$ for low values of pD. Above pD 3.3 only the 1590 cm.$^{-1}$ peak remains. Similar behavior is observed for the manganese(II) and the cerium(III)–EDTA complexes.

For the iron(III)–EDTA chelate only a single peak is observed above pD 2.4. This peak has a constant area, but decreases in frequency as the pD is increased (Fig. 4). Conversely, the aluminum chelate has several peaks (Fig. 5). At low pD values peaks are observed at 1720 cm.$^{-1}$ and at 1655 cm.$^{-1}$; with increasing pD, the 1720 cm.$^{-1}$ peak disappears, leaving the 1650 cm.$^{-1}$ peak plus a new peak at 1580–1590 cm.$^{-1}$ which is characteristic of the ionic carboxylate group. The ratio of the areas of these latter two peaks remains constant between pD 2.8 and pD 9.4. Above pD 9.4
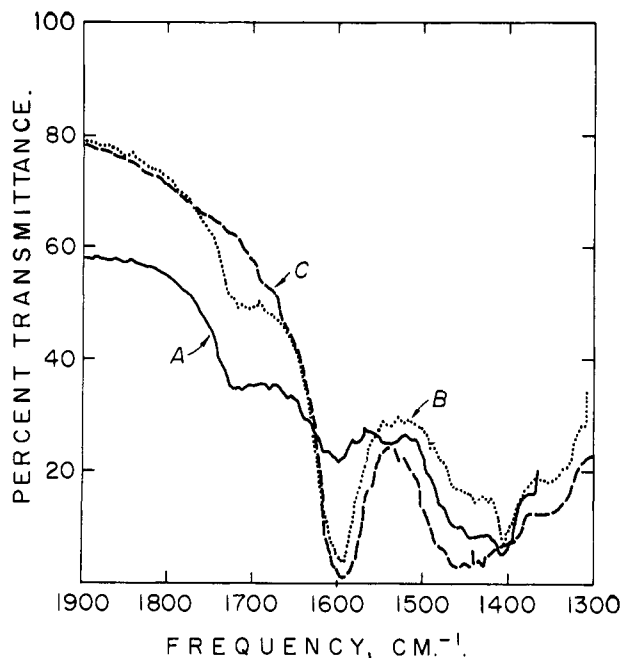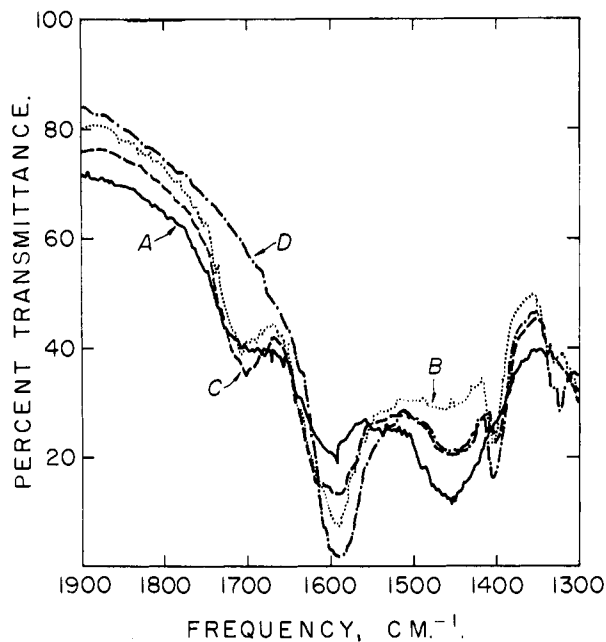
the area of the 1590 cm.$^{-1}$ peak increases at the expense of the 1650 cm.$^{-1}$ peak.

Spectra also have been recorded as a function of pD for the metal–EDTA complexes of chromium(III), vanadium(IV), bismuth(III), and thorium(IV). For chromium the spectra are somewhat similar to those for the alkaline earths with bands at 1720, 1625, and 1580 cm.$^{-1}$. The 1720 cm.$^{-1}$ band disappears for solutions more basic than pD 2.5. The 1625 cm.$^{-1}$ peak grows to maximum area at pD 4.3; as the pD increases further this peak decreases in area as the 1580
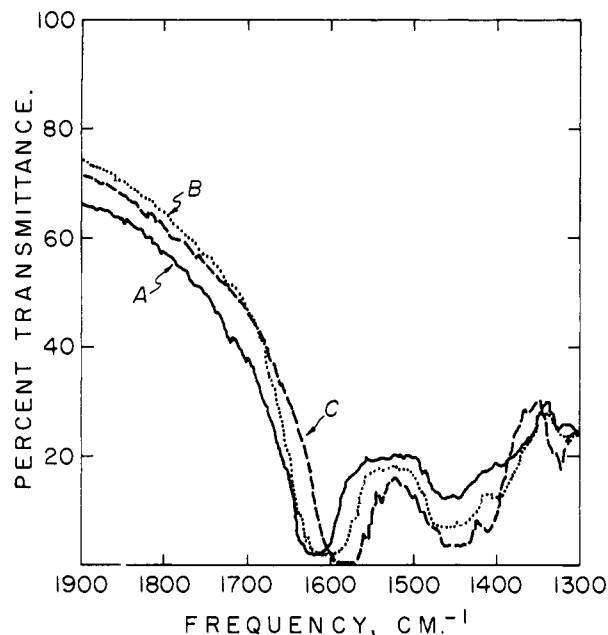
Fig. 4.—Spectra for 0.05 F iron(III)-EDTA in D_2O as a function of solution acidity.

Curve	A	B	C
pD	1.5	8.4	11.0

cm.$^{-1}$ peak grows in area. The two peaks become equal in area at pD 7.9. The vanadium(IV) complex has absorption maxima at 1720 and 1620 cm.$^{-1}$ for pD below 3.6 and the 1620 cm.$^{-1}$ band exists alone up to pH 5.6. Above the latter pD, peaks at both 1620 cm.$^{-1}$ and 1580 cm.$^{-1}$ are observed with their areas becoming equal at pD 7.1. The bismuth(III) chelate forms at low values of pD and the single 1605 cm.$^{-1}$ peak reaches its maximum area at pD 1.0; the area and the frequency for this peak remain constant until pD 11.9, when precipitation of bismuth oxide occurs giving the free EDTA anion and a shift in the peak to 1580 cm.$^{-1}$. Thorium(IV) behaves analogously to the bismuth chelate except the peak is at its maximum area at a pD of about 0.5.

A previous study[2] of the acid salts of EDTA has indicated a molar sensitivity of 28.5 area units per COO^- group (or $NHCH_2COO^-$ group) is obtained for a 0.05 F solution in D_2O. A similar set of area measurements for the EDTA complexes of the alkaline earth ions (Fig. 1) and the divalent metal ions of cobalt, nickel, copper, zinc, cadmium, and lead (Fig. 2) gives an average molar sensitivity of 26.3 ± 2.4 units per molar carboxylate group.

Discussion and Conclusions

The spectra shown in Fig. 1, 2, 3, 4, and 5 have three or fewer absorption peaks depending upon the solution pD. The band at 1710-1720 cm.$^{-1}$ is characteristic of the carboxylic acid group[4] and is the assignment used here. Absorption in the region of 1580-1590 cm.$^{-1}$ is common for ionic carboxylate groups[4]; such an assignment is indicated for the majority of the chelates studied here. The preceding paper in this series[2] discusses the assignment for the 1620 cm.$^{-1}$ absorption band and demonstrates that it can be assigned to a carboxylate group attached to a protonated nitrogen atom, the so-called "zwitterion." In other words, the absorption frequency for the carboxylate group is increased due to the presence of a proton on the nitrogen

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 161-177, 243-274.
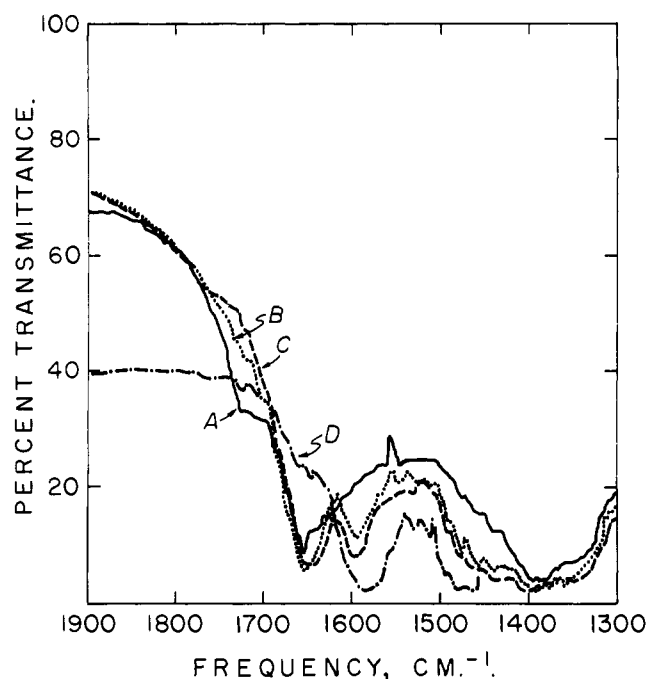

Fig. 5.—Spectra for 0.05 F aluminum-EDTA in D_2O as a function of solution acidity.

Curve	A	B	C	D
pD	2.0	3.2	10.2	12.3

atom of the EDTA molecule. A similar assignment for the 1620 cm.$^{-1}$ absorption bands of the metal-EDTA chelates appears satisfactory in many cases.

TABLE I
INFRARED CHARACTERISTICS OF METAL-EDTA CHELATES IN SOLUTION

A. Alkaline earth-EDTA chelates; 1620 cm.$^{-1}$ peak equals in area 1580 cm.$^{-1}$ peak

Metal ion	pD
Mg	4.9
Ca	4.1
Sr	5.1
Ba	5.8

B. Divalent metal-EDTA chelates; 1590-1600 cm.$^{-1}$ peak equals three-eighths its maximum area

Ion	pD	log K^M_{MHY} (exptl.)	log K^M_{MHY} (lit.)[6]	Diff.
Co	1.6	8.5	9.1	−0.6
Ni	1.1	9.8	11.5	−1.7
Cu	1.3	9.2	11.5	−2.3
Zn	1.4	9.0	9.3	−0.3
Cd	1.5	8.8	9.1	−0.3
Pb	1.2	9.5	10.6	−1.1

Thus, the alkaline earth chelates give spectra under basic conditions (curve D, Fig. 1) which are virtually identical with the spectra for the EDTA anion, Y^{-4}.[2] As the solutions for these chelates are acidified, a peak at 1620 cm.$^{-1}$ appears which is analogous to that for the EDTA species H_2Y^{-2}. Table I, part A, indicates the conditions where the areas of the 1620 and 1580 cm.$^{-1}$ peaks are equal; for the EDTA anion this condition occurs at pD 8.4,[2] where the monoprotonated form of EDTA, HY^{-3}, is the major species in solution. (Although the protonated forms of the EDTA anion in D_2O solutions will contain mainly deuterium atoms rather than hydrogen atoms, the more familiar symbolism is used here.) Therefore, it appears logical to conclude that the pD's listed in Table I, part A,

give the conditions where MHY^- is the major complex species in solution. Also, the existence of a 1620 cm.$^{-1}$ peak indicates that the proton is on one of the nitrogen atoms and not on a carboxylate group. Hence the alkaline earth ions do not compete effectively with protons for the nitrogen atoms of EDTA. The presence of such metal ions inhibits attachment of a proton to more acidic conditions, showing some metal–nitrogen coordination, but does not prevent such attachment. At lower pD the 1620 cm.$^{-1}$ peak is the only peak observed. Under these conditions (curve B, Fig. 1) MH_2Y should be the major complex species, but dissociation probably occurs to a great extent, yielding H_2Y^{-2}, which also shows a 1620 cm.$^{-1}$ peak.[2]

In the case of the other divalent ions studied, a peak at 1620 cm.$^{-1}$ is not observed. The only peaks observed were at 1720 cm.$^{-1}$ (due to a carboxylic acid group) and at 1590–1600 cm.$^{-1}$ without an intermediate peak. Since Schwarzenbach, Gut, and Anderegg have shown that these metal complexes protonate in acid solutions, the absence of a 1620 cm.$^{-1}$ peak under all conditions of acidity at which the complex is formed (Fig. 2) indicates that the proton does not add to the nitrogen, but to the carboxylate groups. Hence, this is believed to be strong evidence that the divalent ions of cobalt, nickel, copper, zinc, cadmium, and lead form strong metal–nitrogen bonds with the EDTA ligand.

If the 1590–1600 cm.$^{-1}$ peak is due to the protonated chelate species at lower pD's then the solution acidity where this peak equals three-eighths its maximum value represents the condition where the chelate concentration equals the concentration of free metal ion. This assumes MHY^- shows a peak for one carboxyl group at 1720 cm.$^{-1}$ and a peak for three carboxylate groups at 1590–1600 cm.$^{-1}$, while MY^{-2} shows a peak for four carboxylate groups at 1590–1600 cm.$^{-1}$. This situation at lower pD's can be expressed by the reaction

$$M^{+2} + H_3Y^- \longrightarrow MHY^- + 2H^+; \quad K = K^M_{MHY}/K_2K_3 \quad (1)$$
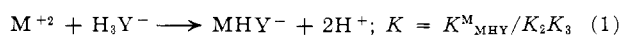
where K^M_{MHY} is the stability constant for the reaction $MHY^- \rightarrow M^{+2} + HY^{-3}$ and K_2 and K_3 are dissociation constants for EDTA. Part B of Table I gives the corrected values for pD at the condition where the area is equal to three-eighths its maximum value for 0.05 F solutions of the metal–EDTA complexes. By substituting the corrected concentrations of H_3Y^- and of H^+ into eq. 1 the values of K^M_{MHY} can be calculated; the resulting values are given in part B, Table I, together with the literature values. To determine the true H_3Y^- concentration, the dissociation constants of EDTA must be corrected for D_2O solutions. This can be done by using the equations proposed by Li, Tang, and Mathur[5] for carboxylic and amino acids in D_2O; the calculated pK's are: pK_1, 2.3; pK_2, 3.1; pK_3, 7.0; pK_4, 11.7. Although this technique should not yield exact stability constants, some of the differences in the calculated values of K^M_{MHY} and the literature values are due to an isotope effect from the D_2O solution.

The mercury(II)–EDTA chelate exhibits somewhat unique infrared behavior; below pD 3.6 three bands at 1700, 1615, and 1590 cm.$^{-1}$ are observed. At pD 3.6 the area of the 1590 cm.$^{-1}$ peak is three times as great as that for the 1615 cm.$^{-1}$ peak and the 1700 cm.$^{-1}$ peak has disappeared. This would be the condition expected if equal concentrations of HgY^{-2} and $HgHY^-$ existed with the proton on the nitrogen atom of the EDTA ligand. Then the 1620 cm.$^{-1}$ peak would be due to a "zwitterion" for two of the four carboxylate groups for the species $HgHY^-$. Making this assumption, the pD would be equal to log K^M_{MHY} for the mer-

(5) N. C. Li, P. Tang, and R. Mathur, *J. Phys. Chem.*, **65**, 1074 (1961).

cury–EDTA complex; the literature value is 3.06.[6] A pD of 3.6 is not surprising in view of the use of D_2O solutions and the attendant isotope effect.

The chromium(III) complex also appears to have a proton on the nitrogen atom in view of the 1620 cm.$^{-1}$ peak. However, the high positive charge of this metal ion might bring about a large shift in the carboxylate peak and thus account for the 1620 cm.$^{-1}$ frequency. This seems probable, especially in view of the strong tendency for chromium(III) to coordinate with nitrogen. Addition of a hydroxide ion to the metal ion would lower its charge and lessen its effect on the carboxylate frequency. At pD 7.9 the area of this 1620 cm.$^{-1}$ peak equals that of the 1580 cm.$^{-1}$ peak. Schwarzenbach and Biedermann[7] have proposed the equilibrium

$$CrY^- \cdot H_2O \longrightarrow CrY(OH)^{-2} + H^+; \quad -\log K = 7.5 \quad (2)$$
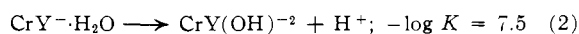
from potentiometric titration data. If the 1620 cm.$^{-1}$ peak and the 1580 cm.$^{-1}$ peak correspond to the two species, then a pD of 7.9 is in reasonable agreement with their value for $-\log K$.

For the iron(III)–EDTA complex the two peaks at 1720 and 1615 cm.$^{-1}$ for pD below 1.9 appear to correspond to two forms of the chelate (Fig. 4). The 1720 cm.$^{-1}$ peak must be due to a proton on a carboxylate group, while the 1615 cm.$^{-1}$ peak may be due to a proton on one of the nitrogen atoms. The latter peak is the only absorption band from pD 2.4 to 7.5. From pD 7.5 to pD 9.5 there is a single peak at 1600 cm.$^{-1}$ and above pD 9.5 the peak is at 1580 cm.$^{-1}$. Schwarzenbach and Heller[8] have proposed the three species of FeY^-, $FeY(OH)^{-2}$, and $FeY(OH)_2^{-3}$ on the basis of pH measurements and potentiometric titrations. From this, the 1615, 1600, and 1590 cm.$^{-1}$ peaks would correspond to these three species, respectively. Then the 1720 cm.$^{-1}$ peak probably would be due to a species $FeHY$ with the proton on a carboxylate group. The bonding between the iron(III) ion and the ligand must be sufficiently strong to raise the carboxylate frequency to 1615 cm.$^{-1}$ under the acidic conditions where FeY^- is thought to exist. Formation of $FeY(OH)^{-2}$ and $FeY(OH)_2^{-3}$ causes the frequency to become proportionally lower.

The aluminum–EDTA complex also has a somewhat unique set of spectra (Fig. 5) and appears to have some distinct structural features Below pD 2.5 a small peak is observed at 1720 cm.$^{-1}$, which is undoubtedly due to a proton on a carboxylate group, plus a peak at 1640 cm.$^{-1}$. From pD 3 to pD 9.4 this peak has a constant area and a constant frequency. A peak at 1590 cm.$^{-1}$ begins to appear at pD 2.5 and reaches a maximum area at pD 3. This area remains constant until pD 9.4 where it increases at the expense of the 1640 cm.$^{-1}$ peak. The frequency decreases slowly to 1580 cm.$^{-1}$ as the pD is raised. The ratio of the area of the 1640 cm.$^{-1}$ peak relative to that of the 1590 cm.$^{-1}$ is 0.60 from pD 3 to pD 9.4. Because the known stability constants for the aluminum–EDTA indicate that AlY^- is the species present for this pD range,[9] the actual structure must include this simplified form. One possible structure would involve a dimer, $Al_2Y_2^{-2}$, with five of the eight carboxylate groups covalently bonded to the two aluminum ions and bringing about the 1640 cm.$^{-1}$ peak. The remaining three carboxylate groups could either be ionically bonded or be free and bring about the absorption band. An alternative,

(6) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

(7) G. Schwarzenbach and W. Biedermann, *ibid.*, **31**, 459 (1948).

(8) G. Schwarzenbach and J. Heller, *ibid.*, **34**, 576 (1951).

(9) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," Part I, Organic Ligands, Special Publication No. 6, The Chemical Society, London, 1957.

and somewhat more plausible, explanation of the two peaks observed for aluminum–EDTA would be that the area measurements are in error or that the molar absorptivities are different for the two species and that the ratio of concentrations for the two species is unity. Making this assumption, a possible structure for the complex would be $AlHY(OH)^-$ with a proton attached to one of the nitrogen atoms. This, plus strong coordination with the two attached carboxylate groups, might account for the 1640 cm.$^{-1}$ peak, while the other two carboxylates could bring about the 1580 cm.$^{-1}$ peak. Studies of the n.m.r. spectra for the protons in the aluminum–EDTA complex[10] tend to support this latter conclusion. A dimeric form of the chelate may be the actual species in solution with a structure represented by
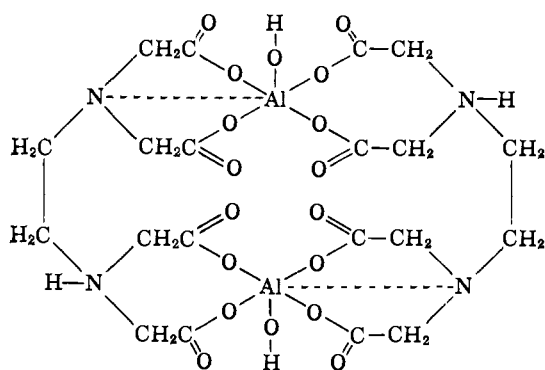
Such a structure would explain in part the slow equilibria observed for the aluminum–EDTA complex

(10) D. T. Sawyer, R. J. Kula, C. M. Finley, and S. Chan, unpublished results, in preparation (1962).

and the resulting difficulties when titrating aluminum ions with EDTA. An alternative, but comparable structure would be a linear polymer. The infrared data (Fig. 5) indicate that at about pD 10 the complex becomes unstable and aluminum hydroxide precipitates, leaving the EDTA anion. The n.m.r. data also support this conclusion.[10]

The cerium(III)–EDTA complex has peaks only at 1610 and 1590 cm.$^{-1}$ above pD 2.3. Since the peak areas are difficult to measure, further conclusions concerning the structure are not justified.

For the vanadium(IV)–EDTA complex there is a 1720 cm.$^{-1}$ peak up to pD 3.6. There also is a 1620 cm.$^{-1}$ peak which reaches its maximum area at pD 3.6 and then decreases in area as a 1580 cm.$^{-1}$ peak increases in area. The areas of these two peaks are equal at pD 7.1. At this condition the chelate species may have the structure $VOHY(OH)^{-2}$ with the proton on one of the nitrogen atoms. As the pD is increased, this proton would be removed causing all four carboxylates to absorb at 1580 cm.$^{-1}$.

From pD 1 to pD 12 the bismuth–EDTA complex gives a single peak at 1605 cm.$^{-1}$ which would indicate a single chelate species of the form BiY^- without protons on the nitrogen atoms. Because the frequency for this chelate is above 1580 cm.$^{-1}$, which is characteristic of the free carboxylate group, the strong coordinate bonding is indicated with some possibility that the nitrogen atoms are also strongly coordinated. The same remarks are applicable for the thorium(IV)–EDTA complex except that it has a single peak at 1605 cm.$^{-1}$ from pD 0.4 to pD 12. Again, strong coordinate bonding is indicated.

Metal Salts and Complexes of Dialkoxyphosphonylacetylmethanide Ions[1]

By F. A. Cotton[2] and R. A. Schunn

The preparation and characterization of some compounds containing the anions $[(RO)_2P(O)CHCOCH_3]^-$ are reported. Denoting the anion with R = C_2H_5 as L, the compounds prepared are: NaL, CrL_3, $(CoL_2)_x$, and ZnL_2. The cobalt complex is a pale pink solid containing octahedrally coordinated cobalt and evidently involves association of CoL_2 molecules. Association persists in various organic solutions at high concentrations, but dissociation to give a blue species, which may be a tetrahedral monomer, has been observed. The analog of CrL_3 in which L = CH_4 has also been prepared as have $\{[(EtO)_2P(O)]_2CH\}K$ and $[(EtO)_2P(O)]_2CHCH_3$, the latter by reaction of methyl iodide with the sodium salt $\{[(EtO)_2P(O)]_2CH\}Na$. The postulated structures of all diamagnetic compounds have been confirmed by high resolution proton magnetic resonance spectroscopy. Finally, it is shown that several lines of physical evidence leave little doubt that resonance similar to that in β-ketoenolate anions occurs in both the $\{[(EtO)_2P(O)]_2CH\}^-$ and $[(EtO)_2P(O)CHCOCH_3]^-$ anions.

Introduction

A considerable amount of work has been reported in the early literature on the existence of enol forms of β-ketophosphonates, $(RO)_2P(O)CH_2COR'$. However, in 1952, Perkow[3] showed that many of the β-ketophosphonates believed to exist in enol as well as keto forms were in reality mixtures of the β-ketophosphonates and the isomeric vinyl phosphates, $(RO)_2P(O)OCR'=CR_2$. This subject has recently been reviewed by Lichtenthaler.[4]

In many cases the two isomers can be cleanly separated and such is the case for the dialkoxyphosphonylacetylmethanes, $(RO)_2P(O)CH_2COCH_3$, where R = CH_3 or CH_2CH_3. Pudovik,[5] in 1957, reported the reaction of diethoxyphosphonylacetylmethane with sodium metal and subsequent reaction of the mixture with various organic halides to give products of the type $(C_2H_5O)_2P(O)CHRCOCH_3$. The intermediate sodium compound was not isolated. The intermediate position of diethoxyphosphonylacetylmethane between acetylacetone and bis-(diethoxyphosphonyl)-methane, which we have recently investigated,[6] made it appear

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(3) W. Perkow, K. Ullerick, and F. Meyer, Naturwissenschaften, 39, 353 (1952).

(4) F. W. Lichtenthaler, Chem. Rev., 61, 607 (1961).

(5) A. N. Pudovik, et al., Zhur. Obschei. Khim., 27, 2367 (1957); Chem. Abstr., 52, 71341 (1958).