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Properties and Infrared Spectra of Ethylenediaminetetraacetic Acid Complexes. I. Alkaline Earth Chelates¹

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The infrared spectra of the solid ethylenediaminetetraacetic acid chelates of the alkaline earths indicate that the relative stabilities for the complexes are: $Mg > Ca > Sr > Ba$. Studies of the spectra, when related to other data, lead to the conclusion that the bonding is primarily ionic. The sodium salts of these compounds have been synthesized and isolated.

The complexes formed between the ions of the alkaline earths and ethylenediaminetetraacetic acid (hereafter referred to as EDTA) have been studied extensively in terms of their properties in solution.²⁻⁵ Although the ability of EDTA to form stable complexes in solution with $Mg(II)$, $Ca(II)$, $Sr(II)$ and $Ba(II)$ is firmly established, little is known of the properties of these materials in the solid phase. Also, the nature of the bonding, both in solution and in the solid phase, has not been established. There is still disagreement regarding the coordination number for both the metal ions and the EDTA ligand.⁶

The interactions between the alkaline earth ions, and the nitrogen and oxygen atoms of the EDTA anion would be expected to be essentially electrostatic,^{2,7} but data are not available to establish this conclusively. Busch and Bailar⁸ have used the infrared technique to determine whether the bonding is covalent or ionic for $Co(III)$ -EDTA complexes. Their data indicate that as the bonding of the carboxylates becomes more covalent the absorption band for the free carbonyl bond ($C=O$) of the carboxylate groups shifts to higher frequencies. It is reasoned that covalent bonding of the metal ion localizes the electrons around the free carbonyl group and increases the double bond character causing an increase in the absorption frequency. More recent work^{9,10} also has given support to a relationship between the infrared absorption spectra and the type of bonding.

Although these workers have suggested that the coordination number of metal ions and ligands can often be determined from the infrared spectra, our data indicate that there are serious limitations for many cases. The results of an investigation of the infrared spectra of the chelates of EDTA with the ions of the alkaline earth elements are presented below. These studies were carried out using the KBr disk technique.

Experimental

Infrared Spectra.—The infrared spectra were recorded

(1) This research was supported by a grant-in-aid from the Research Corporation.

(2) R. A. Care and L. A. K. Staveley, *J. Chem. Soc.*, 4571 (1956).

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

(4) G. Schwarzenbach and H. Ackermann, *ibid.*, **31**, 1029 (1948).

(5) R. W. Schmid and C. N. Reilley, *THIS JOURNAL*, **78**, 5513 (1956).

(6) J. C. Bailar, Jr., "The Chemistry of the Coordination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, p. 778.

(7) *Ref.* 6, p. 176, 177.

(8) D. H. Busch and J. C. Bailar, Jr., *THIS JOURNAL*, **75**, 4574 (1953).

(9) M. L. Morris and D. H. Busch, *ibid.*, **78**, 5178 (1956).

(10) S. Kirschner, *ibid.*, **78**, 2372 (1956).

with a Perkin-Elmer model 21 recording spectrophotometer equipped with a sodium chloride prism. The solid complexes were pressed into disks¹¹ using KBr as the diluent. Approximately 1-3 mg. of the chelate was mixed with 500 mg. of KBr for each disk.

Reagents.—The inorganic salts, acids and bases used in preparing the complexes were reagent grade in all cases. The disodium salt of EDTA (purchased from Matheson, Coleman and Bell) was used in preparing the complexes and salts of EDTA. The tetraacid of EDTA was also obtained from Matheson, Coleman and Bell.

Preparation of Disodium Salts of the EDTA Complexes of the Alkaline Earth Ions.—The following inorganic salts were used in preparing solid chelates: $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$. To a solution of 0.062 mole of the alkaline earth salt in 50 ml. was added 0.062 mole of disodium dihydrogen ethylenediaminetetraacetate ($Na_2H_2EDTA \cdot 2H_2O$) dissolved in 100 ml. of H_2O . The two hydrogen ions released from the ligand were neutralized by adding 0.124 mole of $NaHCO_3$ to the solution. The resulting solution was adjusted to pH 7 with HCl and warmed almost to the boiling point; then absolute ethanol was added until a slight turbidity appeared. In some cases it was necessary to evaporate the solution and pour it into 500 ml. of absolute ethanol to bring about crystallization. Finally, the solution was cooled in an ice-bath; a pure white crystalline material separated from the solution for each of the alkaline earths. After filtering the crystals from the solution, they were recrystallized from a water-ethanol mixture. The recrystallized complexes were immediately placed in a vacuum desiccator for 72 hours.

1. $Na_2[Mg(C_{10}H_{12}N_2O_8)] \cdot 4H_2O$.—The complex was analyzed for magnesium by precipitating as the 8-hydroxyquinolate after combustion of the chelate at 900°. *Anal.* Calcd. for complex: C, 27.89; H, 4.68; Mg, 5.65. Found: C, 28.77; H, 5.32; Mg, 5.69.

2. $Na_2[Ca(C_{10}H_{12}N_2O_8)] \cdot 3.5H_2O$.—The complex was analyzed for calcium by permanganate titration of its oxalate. The chelate was ignited to 900° prior to precipitation of the calcium oxalate. *Anal.* Calcd. for complex: C, 27.46; H, 4.38; Ca, 9.16. Found: C, 27.74; H, 4.57; Ca, 9.15.

3. $Na_2[Sr(C_{10}H_{12}N_2O_8)] \cdot 5H_2O$.—The complex was analyzed for strontium by precipitating as the sulfate after ignition of the chelate at 900°. *Anal.* Calcd. for complex: C, 23.46; H, 4.33; Sr, 17.12. Found: C, 22.82; H, 3.98; Sr, 16.70.

4. $Na_2[Ba(C_{10}H_{12}N_2O_8)] \cdot 1.5H_2O$.—The complex was analyzed for barium by precipitating as the sulfate after ignition of the chelate at 900°. *Anal.* Calcd. for complex: C, 24.09; H, 3.03; Ba, 27.55. Found: C, 24.85; H, 4.00; Ba, 27.58.

Preparation of Trisodium Hydrogen EDTA, Tetrasodium EDTA and Tetrapotassium EDTA.—Equimolar quantities of $Na_2H_2EDTA \cdot 2H_2O$ and NaOH (0.062 mole of each) were mixed in 100 ml. of solution. The solution was heated almost to boiling, then absolute ethanol was added until a slight turbidity appeared in the solution; the resulting solution was placed in ice for several hours. Fine white crystals separated from the solution; these were filtered from the solution and recrystallized from a water-ethanol mixture. The trisodium salt was placed in a vacuum desiccator for 72 hours. The tetrasodium salt of EDTA was prepared in a similar manner, except a large excess of sodium hydroxide (0.3 mole) was added to 0.062 mole of $Na_2H_2EDTA \cdot 2H_2O$. The large excess was necessary to prevent hydrolysis of the resulting tetrasodium salt. The salt was separated in the

(11) M. M. Stimson and M. J. O'Donnell, *ibid.*, **74**, 1805 (1952).

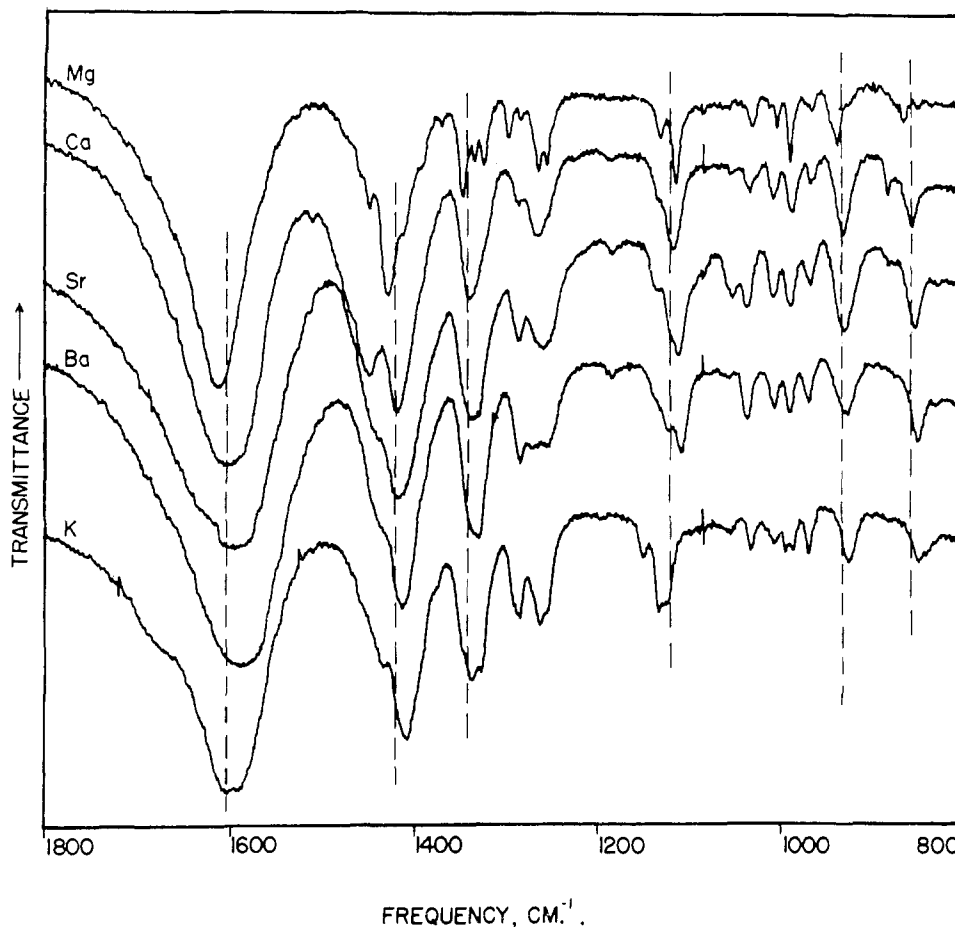


Fig. 1.—Infrared spectra of the EDTA chelates of the alkaline earth ions and of the tetrapotassium salt of EDTA: **Mg**, $\text{Na}_2[\text{Mg}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)] \cdot 4\text{H}_2\text{O}$; **Ca**, $\text{Na}_2[\text{Ca}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)] \cdot 3.5\text{H}_2\text{O}$; **Sr**, $\text{Na}_2[\text{Sr}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)] \cdot 5\text{H}_2\text{O}$; **Ba**, $\text{Na}_2[\text{Ba}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)] \cdot 1.5\text{H}_2\text{O}$; **K**, $\text{K}_4(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)$.

same manner as the trisodium salt. It was not recrystallized in order to prevent hydrolysis. The separated tetrasodium salt was placed in a vacuum desiccator for 72 hours. The tetrapotassium salt was prepared by mixing 0.062 mole of the tetraacid of EDTA with a large excess of KOH, and treating in a similar way to the preparation of the tetrasodium salt. These three salts were analyzed by titration with standardized hydrochloric acid to the dihydrogen salt. *Anal.* Calcd. for $\text{Na}_3(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8) \cdot 5\text{H}_2\text{O}$: equiv. wt., 448. Found: equiv. wt., 451. Calcd. for $\text{Na}_4(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8) \cdot 0.5\text{H}_2\text{O}$: equiv. wt., 194.2. Found: equiv. wt., 193.5. Calcd. for $\text{K}_4(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)$: equiv. wt., 245. Found: equiv. wt., 241.

Results and Discussion

The infrared spectra for the four alkaline earth chelates of EDTA and the tetrapotassium salt of EDTA are shown in Fig. 1. Guide lines have been placed to emphasize the shifts of the major peaks.

In Table I assignments and wave numbers are given for the important peaks of the alkaline earth chelates and the various salts of EDTA. (For reference the peaks of sodium acetate are also given.) The band at 2800–3000 cm^{-1} is due to C–H stretching in the CH_2 groups.¹² The carboxyl groups give a strong band at 1675–1690 cm^{-1} due to C=O stretching; hydrogen bonding causes the frequency to decrease as double bond character

is lost for the COOH group. Previous workers^{8,9,13} have discussed these correlations in some detail, and have also presented data for the band due to C=O stretching in the carboxylate group at 1600 cm^{-1} . It has been demonstrated for Co(III)–EDTA complexes⁹ that a shift of this peak to higher frequencies indicates increased covalent character for the metal–carboxyl bond.

Referring to Table I, the peaks for the COO⁻ groups in the alkaline earth chelates show a decrease of frequency in the order: Mg > Ca > Sr > Ba. This corresponds to a decrease in frequency with increasing ionic radius, and suggests that Mg has the most covalent character of the series and Ba the least. This is in agreement with the general rules favoring covalent bonds,¹⁵ and indicates that the order of increasing stability for the complexes should be Ba < Sr < Ca < Mg.⁷ This conclusion is in agreement with the stability constants determined in solution¹⁶ except Mg and Ca are reversed. The reversal for these ions can be attributed to the

(13) D. H. Busch and J. C. Bailar, Jr., *THIS JOURNAL*, **78**, 716 (1956).

(14) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 140.

(15) *Ref. 14*, p. 209.

(16) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 537.

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

TABLE I
 INFRARED ABSORPTION PEAKS OF ALKALINE EARTH CHELATES AND SALTS OF EDTA^a

	r , Ionic radius	-CH ₂	-COOH	-COO ⁻	-COO ⁻	-COO ⁻	-C-N	-COO ⁻	
Na ₂ MgY·4H ₂ O	0.66	2920(w)		1610(s)	1425	1350 1325(w)	1115(s) 1130	940(s)	865
Na ₂ CaY·3.5H ₂ O	1.01	2840(w)		1605(s)	1420	1340	1120	930(s)	855
Na ₂ SrY·5H ₂ O	1.18	2840(w)		1595(s)	1415	1335	1110	925(s)	850
Na ₂ BaY·1.5H ₂ O	1.34	2830(w)		1590(s)	1410	1330	1105	925(s)	845
H ₄ Y·0.5H ₂ O		3020(w)	1690(s)	1635(vw)	1390(w)	1315(w)	..	965(w)	870(w)
Na ₂ H ₂ Y·2H ₂ O		3020 2770(w)	1675	1630(s)	1395	1320 1365	..	960 940 920	815
Na ₃ HY·5H ₂ O		3030 2810	1675	1625(s)	1400	1320 1365	1125	960 940 920(s) 900	815 845
Na ₄ Y·0.5H ₂ O	0.96	2980(vw) 2800		1600(s)	1410	1330	1120 1135	965 920	845
K ₄ Y	1.33	2800		1595(s)	1405	1330	1120 1130	965 920	845
NaOAc		2990 2940		1580(s)	1430(s)	925(s)	..

^a Abbreviations used in the table: Y, ethylenediaminetetraacetate anion; v, very; w, weak; s, strong; r, ionic radius, ångström units, for the metal ions.^{2,14} Frequencies for peaks are given in wave numbers, cm.⁻¹.

strong tendency for Mg to form hydrate bonds. When the complex is in the solid phase water is not available and Mg becomes the most strongly complexed by EDTA. In light of the observations of Morris and Busch,⁹ there is strong evidence that all of the alkaline earth ions are, to a major degree, bonded ionically to the carboxylate groups of EDTA.

The frequencies for the 1600 cm.⁻¹ band for the sodium-acid salts of EDTA (Na₂H₂EDTA·2H₂O and Na₃HEDTA·5H₂O) indicate that hydrogen bonding increases the double bond character for the COO⁻ group. Some complexing is indicated for the tetrasodium salt, since its frequency is greater than that obtained for the Ba chelate or the tetrapotassium salt. This conclusion is supported by the work of Schwarzenbach and Ackermann³ who have reported a stability constant for the EDTA complex of sodium ion (log *K* = 1.66). Their work indicated that potassium ion is not complexed by EDTA, however, the relatively high frequency for the 1600 cm.⁻¹ band of K₄EDTA (greater than the Ba chelate and equal to the Sr chelate) would indicate that there is some interaction with the ligand.

The data in Table I for the sodium salts of EDTA are in general agreement with the infrared spectra of these salts reported by Chapman.¹⁷ Other peaks for the COO⁻ group are listed in Table I at 1390-1425 cm.⁻¹ and at 1315-1350 cm.⁻¹. These peaks show some splitting and are not as generally useful as those in the 1600 cm.⁻¹ region. However, the trend of lower frequencies with increasing ionic radii is confirmed. Two additional peaks are given in Table I that may be related to the carboxylate group; one at 900-960 cm.⁻¹ and the other at 815-865 cm.⁻¹. These peaks exhibit the same general shift of frequencies, but specific as-

signments are not possible. Bellamy¹² indicates that the COOH group normally gives a peak in the 935 cm.⁻¹ region; this suggests that the bonded carboxylate group might exhibit a similar peak. It should be noted that both of these peaks are in a region where skeletal vibrations are common and definite assignments are not possible.

The remaining peak that is listed in Table I (1100 cm.⁻¹) has been assigned to the C-N bond. Although the C-N group has not been extensively studied by infrared techniques, what data are available indicate a peak in the 1100 cm.⁻¹ region.^{12,13} Kirschner has noted this peak in his studies of Copper(II)-EDTA complexes.¹⁰ The peak is completely absent for the disodium salt of EDTA, and it is proposed that this is due to the formation of "Zwitter" ions in this salt⁶; the closest peak is at 1055 cm.⁻¹. The trisodium salt of EDTA also exhibits the 1055 cm.⁻¹ peak in addition to a peak at 1125 cm.⁻¹; with the tetrasodium salt there is only a peak in the 1100 cm.⁻¹ region. The same trend in frequencies is shown for this peak as takes place for the other groups (decreasing with increasing ionic radii); however, a doublet appears in the case of Mg.

Conclusion

The data indicate that some correlations between the type of bonding and the infrared spectra are possible. A carboxylate peak (C=O stretch) in the region of 1550-1610 cm.⁻¹ indicates that the bonding is primarily ionic; other workers^{8,9,13} have evidence for covalent bonding when this peak is in the 1625-1650 cm.⁻¹ region. When the peak occurs between these two regions the bonding is probably partially ionic and partially covalent. Although Kirschner¹⁰ uses this correlation to support

(18) A. Weissberger, "Technique of Organic Chemistry," Vol. IX, Interscience Publishers, Inc., New York, N. Y., 1956, p. 530.

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

an assignment of six for the coordination number of copper(II)-EDTA chelate, reference to the data for K_4EDTA in Table I shows that it would be difficult to resolve an uncoordinated carboxylate group in the presence of the 1615 cm.^{-1} peak of the copper chelate. Also, the disappearance of the 1718 cm.^{-1} peak only indicates a loss of the proton on the carboxyl group, and does not establish that coordination has occurred with the copper ion. The peaks for the alkaline earth chelates are as sharp as the peak observed for the copper(II) chelate and, hence, it could be concluded that the alkaline earths have a coordination number of six. This would be in agreement with the proposals of other investigators⁶; however, when the data for the sodium and potassium salts of EDTA are noted, it is not possible to conclude that the coordination number is six for the alkaline earth chelates. The data only support the possibility of this coordination number, and do not prove its existence. If an extra peak were present, this would give strong evidence for a coordination number other than six. It is on this latter basis that the infrared method should prove useful in determining coordination numbers.

Care and Staveley² have studied the thermo-

dynamics of the EDTA complexes of the alkaline earths and have made some proposals concerning the bonding between ligand and metal ion. Although their studies were for aqueous systems, the data indicate that the bonding between the carboxylate groups and the metal ion follow the order of strengths suggested by the infrared data: $Mg > Ca > Sr > Ba$. In addition they suggest that the calcium ion has the ideal size for the formation of chelate rings with the nitrogen atoms of EDTA, and thus calcium has the largest stability constant for aqueous EDTA solutions of the alkaline earth ions. This increased stability is attributed to the nitrogen-metal bond, and the data in Table I for the peak assigned to the C-N bond (1120 cm.^{-1}) tend to support their proposal. Considering the major peak of the doublet for magnesium, the order of decreasing frequency (and decreasing bond strength) is $Ca > Mg > Sr > Ba$, which is the order of decreasing stability constants for the EDTA complexes. The tetrasodium salt of EDTA also has a peak at 1120 cm.^{-1} which may not be surprising when it is noted that sodium ion is complexed weakly by EDTA⁸ and has an ionic radius roughly the same as calcium.

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