Wilson[6] as that of $RuCl_2^+$ is somewhat similar to our curve for $RuCl_2^+$ (C). Their molar extinction coefficient at the maximum is very nearly the same but at 270 and 370 mμ their molar extinction coefficient is *ca.* 40% higher and *ca.* 25% lower, respectively, than found here. A mixture of $RuCl_2^+$ (C) and $RuCl_2^+$ (T) would not explain the discrepancies. The previous paper[1] gives two spectra for $RuCl_2^+$; both of these spectra resemble that of $RuCl_2^+$ (C) above 300 mμ. Below 300 mμ the spectrum obtained in 0.2 *M* $HClO_4$ corresponds more closely to that of $RuCl_2^+$(C). Again a mixture of the two isomers would not explain the spectra and it is concluded that additional species were present in the earlier work.

This work was performed under the auspices of the U. S. Atomic Energy Commission.

(6) I. M. Rehn and A. S. Wilson, "Ruthenium (III) Chloride Complexes in Trifluoroacetic Acid Solution," Hanford Atomic Works, Richland, Washington.

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Properties and Infrared Spectra of Ethylenediaminetetraacetic Acid Complexes. III. Chelates of Higher Valent Ions

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Infrared spectra have been recorded for the EDTA chelates of Al(III), Ce(III), Bi(III), V(III), V(IV), Cr(III), Fe(III), Co(III), Ti(IV), Th(IV), Mo(V) and Mo(VI). The spectra, when related to previous studies, indicate that the bonding between ligand and metal ion is primarily ionic for the Al(III), Ce(III) and Bi(III) chelates, and primarily covalent for the remainder of the chelates. Correlations are made between the various functional groups and their resulting absorption peaks. The EDTA chelates for this group of metal ions have been synthesized and isolated.

The complexes formed between the ions of divalent metal ions and ethylenediaminetetraacetic acid (hereafter referred to as EDTA) have been discussed relative to their infrared spectra in the previous two papers of this series.[1,2] Additional infrared studies have been reported for the EDTA chelates of Co(III),[3,4] Cu(II),[5] Pd(II)[6] and Pt(II).[6] The present study is concerned with the infrared spectra of the EDTA chelates of Al(III), Ce(III), Bi(III), V(III), V(IV), Cr(III), Fe(III), Co(III), Ti(IV), Th(IV), Mo(V) and Mo(VI). Although the solution properties for this group of chelates have been studied extensively,[7–9] little is known of their properties in the solid phase.

The previous investigations[1,2] have shown that the bonding is primarily ionic for the EDTA chelates of the divalent metal ions. However, for many of the metal ions considered here the bonding would be expected to be primarily covalent,[10] but with the exception of the Co(III)–EDTA chelate,[3] data are not available to confirm this supposition. Determination of the kind of bonding in EDTA chelates by the use of infrared data has been reviewed previously.[1–3] As the bonding of the carboxylate groups becomes more covalent the absorption peak for the antisymmetrical vibration (or free carbonyl bond, C=O) of the COO^- groups shifts to higher frequencies. Some limitation can be given from infrared data, for the maximum number of EDTA-donor groups involved in chelation but the actual number usually cannot be determined.

Experimental

Infrared Spectra.—The infrared spectra were recorded with a Perkin-Elmer model 21 recording spectrophotometer equipped with a sodium chloride prism. The solid chelates were pressed into disks[11] using KBr as the diluent. Approximately 1–3 mg. of the chelate were 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 as well as the tetraacid of EDTA (both purchased from J. T. Baker Co.) were used in preparing the solid chelates. *p*H titrations indicated that these materials were essentially pure. The preparation and analysis of tetrasodium-EDTA has been discussed previously.[1]

Preparation of the EDTA Complexes of Higher Valent Ions.—The following inorganic salts were used directly in preparing solid chelates: $Ce(NO_3)_3 \cdot 6H_2O$, $BiCl_3 \cdot H_2O$, $VOCl_2$, $CrCl_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Th(NO_3)_4 \cdot 4H_2O$. To a solution of 0.062 mole of the inorganic salt in 50 ml. was added 0.062 mole of disodium dihydrogen ethylenediaminetetraacetic acid ($Na_2H_2EDTA \cdot 2H_2O$) 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 with HCl, $NaHCO_3$ or NaOH to *p*H 3 for the Bi(III) chelate; to *p*H 5 for the Fe(III) chelate; to *p*H 7 for the Ce(III), V(IV) and Cr(III) chelates; and to *p*H 9 for the Th(IV) chelate. The solutions for this group of chelates were evaporated at ambient temperature until the volume for each solution was reduced to about 25 ml. In the case of the Fe(III) chelate, crystals started to form and this solution was placed in an ice bath. For the solution of the V(IV) chelate NaCl crystallized out and was separated prior to placing the solution in an ice bath. Methanol was added to the concentrated solutions of the Ce(III), Bi(III) and Th(IV) chelates and ethanol to the concentrated solution of the Cr(III) chelate to help induce crystallization. These solutions were also placed in an ice bath. The resulting crystalline materials in these

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(1) D. T. Sawyer and P. J. Paulsen, THIS JOURNAL, **80**, 1597 (1958).

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

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

(4) D. H. Busch and J. C. Bailar, Jr., *ibid.*, **75**, 4574 (1953).

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

(6) D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78**, 716 (1956).

(7) J. Bjerrum, G. Schwarzenbach and L. J. Sillén, "Stability Constants," Special Publication No. 6, The Chemical Society, London, 1957, pp. 76–78.

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

(9) S. Chaberek and A. E. Martell, "Organic Sequestering Agents," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 572.

(10) J. C. Bailar, Jr., "The Chemistry of the Coördination Compounds," Reinhold Publishing Corp., New York, N. Y., 1956, pp. 190–219.

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

cooled solutions were filtered and recrystallized from a water-ethanol mixture.

Isolation of the Al(III) chelate was hindered by the extreme solubility of the complex. After combining 0.062 mole of $Al(NO_3)_3 \cdot 9H_2O$ with 0.062 mole of $Na_2H_2EDTA \cdot 2H_2O$ in 150 ml. of H_2O, $NaHCO_3$ was added to bring the solution to *p*H 9. The solution was evaporated at ambient temperature to less than 25 ml. and then placed in an acetone–Dry Ice bath. The resulting material was filtered and washed with a small amount of H_2O. A significant portion of the separated material was insoluble in H_2O. Because of the high solubility and difficulty in separation the chelate was not recrystallized.

The V(III) chelate was prepared by dissolving 0.062 mole of $VOCl_2$ in 50 ml. of H_2O to which was added 0.062 mole of $Na_2H_2EDTA \cdot 2H_2O$ in 100 ml. of H_2O. To this solution was added 0.04 mole of metallic zinc (20 mesh) and the mixture was stirred vigorously for 15 minutes. The resulting brown solution was separated from the remaining zinc metal and approximately 200 ml. of acetone was added to bring about crystallization. The solution then was cooled in an ice bath, and the resulting crystalline material was filtered. Because of the tendency for air oxidation of the V(III) chelate, the material was not recrystallized. Analysis indicated that this chelate contained considerable zinc as an impurity.

The Co(III) chelate was synthesized from 0.062 mole of $CoCl_2 \cdot 6H_2O$ by oxidizing with chlorine in the presence of 0.062 mole of EDTA using the procedure described by Morris and Busch.[3] The oxidation was carried out in an acetate-acetic acid buffer at *p*H 4. The chlorine oxidation was continued for 6 hours at 0°; then the solution was allowed to stand for 12 hours. The solution was evaporated at room temperature until crystals began to form; next it was cooled in ice and the crystals separated by filtration. The resulting material was recrystallized from water.

Synthesis of the Ti(IV) chelate was accomplished by adding 0.13 mole of $TiCl_4$ to 50 ml. of H_2O. The resulting precipitate of TiO_2 was coagulated by the addition of a small amount of NaOH, filtered, and repeatedly washed with H_2O. The collected precipitate of TiO_2 was added to a 150 ml. solution containing 0.13 mole of ethylenediaminetetraacetic acid (H_4EDTA). The resulting mixture was heated on a steam bath for 4–5 hours and filtered to remove undissolved TiO_2. The filtrate was evaporated at room temperature until crystals appeared, cooled in an ice bath, and the resulting crystalline material separated by filtration. The separated chelate was recrystallized from H_2O.

The preparation of the Mo(V) and Mo(VI) chelates has been described previously.[12] All of the complexes were placed in a vacuum desiccator for at least 72 hours.

1. **$Na[Al(C_{10}H_{12}N_2O_8)] \cdot xH_2O$**.—The complex was analyzed for aluminum by combustion of the solid chelate at 1100° and weighing the residue. The ignited chelate was also analyzed for aluminum by EDTA titration and by precipitation as Al_2O_3. The high value for the aluminum content confirms that the isolated chelate contains a significant portion of $Al(OH)_3$. Although the C–H analysis is far less than the theoretical composition, the presence of a significant amount of carbon supports the conclusion that an EDTA complex has been isolated. Previous work[7–9] and *p*H measurements support the proposal that the isolated material is the sodium salt of the one-to-one complex.

Anal. Calcd. for complex assuming two waters of hydration: C, 32.05; H, 4.30; Al, 7.22. Found: C, 11.48; H, 3.09; Al, 14.6.

2. **$Na[Ce(C_{10}H_{12}N_2O_8)] \cdot 2H_2O$**.—The complex was analyzed for cerium by oxidizing to Ce(IV) with $NaBiO_3$ after combustion of the chelate at 900°. The Ce(IV) solution was filtered and titrated with a standardized ferrous solution to a ferroin end-point.

Anal. Calcd. for complex: C, 24.65; H, 3.31; Ce, 28.80. Found: C, 25.30; H, 3.90; Ce, 28.3.

3. **$Na[Bi(C_{10}H_{12}N_2O_8)] \cdot 2H_2O$**.—The complex was analyzed for bismuth by combustion of the solid chelate at 900° and weighing the residue. The combusted chelate was also analyzed gravimetrically as BiOCl and volumetrically by EDTA titration.

Anal. Calcd. for complex: C, 21.67; H, 2.90; Bi, 37.60. Found: C, 23.60; H, 3.38; Bi, 36.1.

4. **$Na[V(C_{10}H_{12}N_2O_8)] \cdot 5H_2O$**.—The complex was analyzed for vanadium polarographically at *p*H 6 in 0.1 *F* EDTA. Because the V(III) was obtained by zinc reduction, Zn(II) is present as a major impurity; hence the vanadium analysis is low. The C–H analysis is not significantly affected because of the similarity in atomic weight between V and Zn.

Anal. Calcd. for complex assuming five waters of hydration: C, 26.59; H, 4.91; V, 11.26. Found: C, 26.21; H, 4.55; V, 5.9.

5. **$Na_2[VO(C_{10}H_{12}N_2O_8)] \cdot 5H_2O$**.—The complex was analyzed for vanadium polarographically at *p*H 9.5 in 0.1 *F* EDTA.

Anal. Calcd. for complex: C, 24.43; H, 4.52; V, 10.36. Found: C, 24.62; H, 4.66; V, 8.7.

6. **$Na[Cr(C_{10}H_{12}N_2O_8)] \cdot 2H_2O$**.—The complex was analyzed for chromium by oxidizing to Cr(VI) with Na_2O_2 after combustion of the chelate at 900°. The Cr(VI) was titrated with a standardized ferrous solution to a potentiometric end-point.

Anal. Calcd. for complex: C, 30.08; H, 4.04; Cr, 13.03. Found: C, 29.85; H, 4.20; Cr, 11.4.

7. **$Na[Fe(C_{10}H_{12}N_2O_8)] \cdot H_2O$**.—The complex was analyzed for iron by titration with dichromate to a diphenylamine sulfonic acid end-point after combustion of the chelate at 900°.

Anal. Calcd. for complex: C, 31.15; H, 3.66; Fe, 14.52. Found: C, 30.76; H, 4.85; Fe, 14.52.

8. **$Na[Co(C_{10}H_{12}N_2O_8)] \cdot 2H_2O$**.—The complex was analyzed for cobalt by electrolysis after combustion of the chelate at 900°.

Anal. Calcd. for complex: C, 29.60; H, 3.97; Co, 14.51. Found: C, 29.10; H, 4.94; Co, 14.58.

9. **$TiO(C_{10}H_{14}N_2O_8) \cdot H_2O$**.—The complex was analyzed for titanium by combustion of the solid chelate at 1200° and weighing the residue as TiO_2. The method of preparation for the chelate probably would cause H_4EDTA to be present as an impurity. Previous work[7–9] as well as the infrared data which are discussed below support the assigned formula.

Anal. Calcd. for complex: C, 32.22; H, 4.33; Ti, 12.89. Found: C, 35.33; H, 4.55; Ti, 11.53.

10. **$Th(C_{10}H_{12}N_2O_8) \cdot 9H_2O$**.—The complex was analyzed for thorium by combustion of the solid chelate at 1100° and weighing the residue as ThO_2.

Anal. Calcd. for complex: C, 17.63; H, 4.47; Th, 34.10. Found: C, 16.79; H, 3.12; Th, 34.10.

11. **$Na[Mo_2O_4(C_{10}H_{12}N_2O_8)] \cdot H_2O$**.—The complex was analyzed for molybdenum by titration with permanganate after combustion of the chelate at 790°. The molybdenum was reduced with a Jones reductor prior to titration.

Anal. Calcd. for complex: C, 19.75; H, 2.32; Mo, 31.56. Found: C, 19.87; H, 2.24; Mo, 31.97.

12. **$Na_4[Mo_2O_6(C_{10}H_{12}N_2O_8)] \cdot 8H_2O$**.—The complex was analyzed for molybdenum by titration with permanganate after combustion at 790°. The molybdenum was reduced with a Jones reductor prior to titration.

Anal. Calcd. for complex: C, 14.19; H, 3.47; Mo, 23.63. Found: C, 14.90; H, 3.42; Mo, 23.76.

Results and Discussion

The infrared spectra for the EDTA chelates of Al(III), Ce(III) and Bi(III) are shown in Fig. 1; the spectrum for the tetrasodium salt of EDTA is shown at the top for reference. Guide lines have been placed to aid in comparing the spectra and the major absorption bands. These three chelates represent trivalent ions which are not transition metals. The spectra for the EDTA chelates of V(III), V(IV), Cr(III), Fe(III) and Co(III) are shown in Fig. 2 and illustrate the infrared characteristics of higher valent ions with unfilled d-subshells. In Fig. 3 are shown the infrared spectra for the EDTA chelates of Ti(IV), Th(IV), Mo(V) and Mo(VI); the molybdenum chelates are unique because there are two metal ions per ligand in the complex.

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(12) R. L. Pecsok and D. T. Sawyer, THIS JOURNAL, **78**, 5496 (1956).

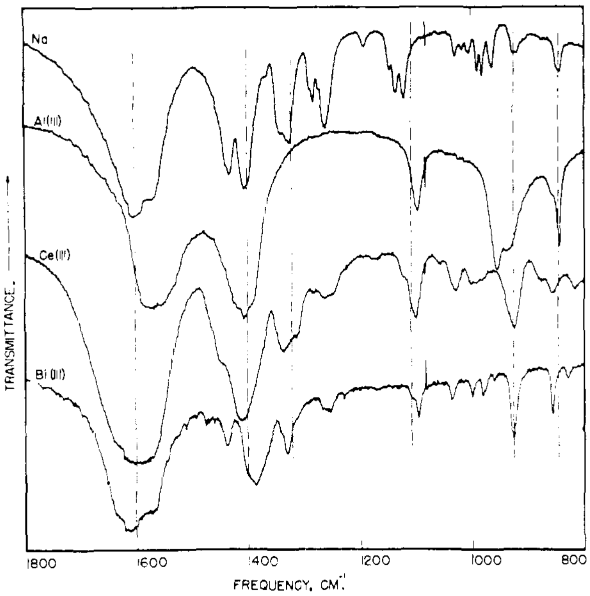

Fig. 1.—Infrared spectra of the EDTA chelates of Al(III), Ce(III) and Bi(III) and of the tetrasodium salt of EDTA: Na, $Na_4(C_{10}H_{12}N_2O_8)\cdot 0.5H_2O$; Al(III), $Na[Al(C_{10}H_{12}N_2O_8]\cdot xH_2O$; Ce(III), $Na[Ce(C_{10}H_{12}N_2O_8)]\cdot 2H_2O$; Bi(III), $Na[Bi(C_{10}H_{12}N_2O_8)]\cdot 2H_2O$.

In Table I assignments and wave numbers are listed for the absorption peaks of the twelve metal-EDTA chelates, and, for comparison, of the tetrasodium salt of EDTA. The ionic and covalent radii for the ions are listed, if known, as well as the stability constants for the chelates.[13,14]

The band at 2800–3000 cm.$^{-1}$ has been assigned previously[1,2,15] to C–H stretching in the CH_2 groups of the EDTA molecule and is observed for all twelve of the chelates listed in Table I. For each of these chelates the frequency of this peak is in the band of 2900–3000 cm.$^{-1}$ and is taken as strong evidence for the formation of a chelate; the acid and sodium-acid salts of EDTA[1] show this peak at 3020–3030 cm.$^{-1}$ while the trisodium and tetrasodium salts absorb at 2800–2810 cm.$^{-1}$. This characteristic frequency for chelated EDTA molecules suggests that the COO^- groups are directly attached to the metal ion. In general, the frequency for the C–H band increases as the ionic radius decreases, which is further evidence that the metal ion has an effect on the frequency of the C–H bond and must be attached to the COO^- groups.

The strongest and most characteristic absorption band for the carboxylate group (COO^-) is in the 1570–1660 cm.$^{-1}$ region and is due to the antisymmetrical vibration of the COO^- group. The first two papers in this series[1,2] have reviewed the correlations between bond character and absorption frequency of the 1600 cm.$^{-1}$ band. The interpretation has been given that as the bonding becomes more ionic the frequency decreases; chelates

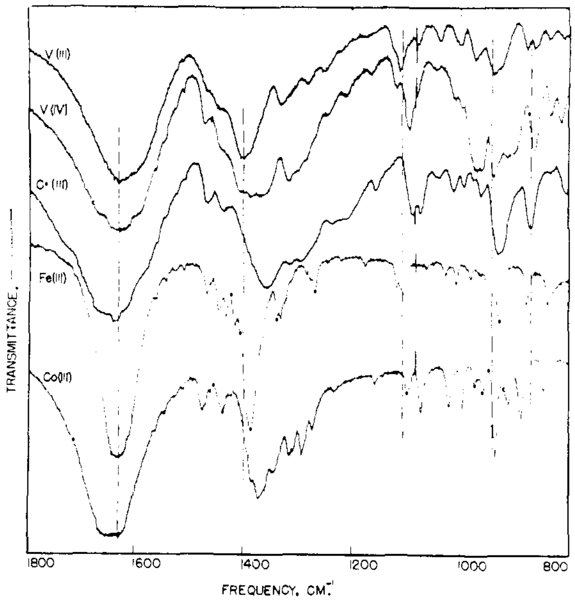

Fig. 2.—Infrared spectra of the EDTA chelates of V(III), V(IV), Cr(III), Fe(III) and Co(III): V(III), $Na[V(C_{10}H_{12}N_2O_8)]\cdot 5H_2O$; V(IV), $Na_2[VO(C_{10}H_{12}N_2O_8)]\cdot 5H_2O$; Cr(III), $Na[Cr(C_{10}H_{12}N_2O_8)]\cdot 2H_2O$; Fe(III), $Na[Fe(C_{10}H_{12}N_2O_8)]\cdot 1H_2O$; Co(III), $Na[Co(C_{10}H_{12}N_2O_8)]\cdot 2H_2O$.

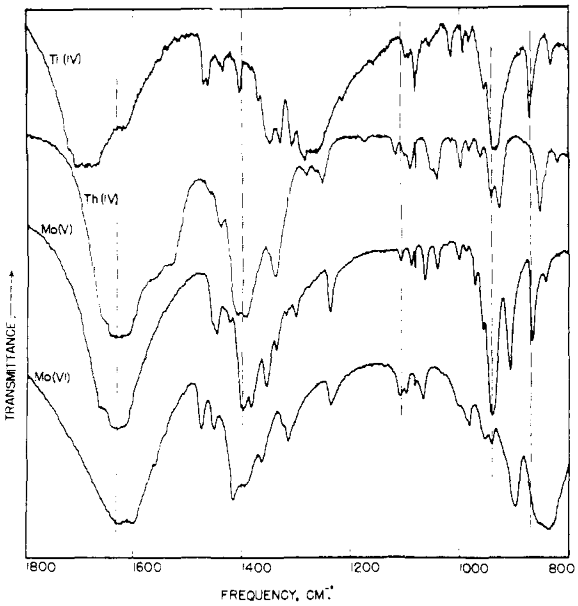

Fig. 3.—Infrared spectra of the EDTA chelates of Ti(IV), Th(IV), Mo(V) and Mo(VI): Ti(IV), $TiO(C_{10}H_{11}N_2O_8)\cdot 1H_2O$; Th(IV), $Th(C_{10}H_{12}N_2O_8)\cdot 9H_2O$; Mo(V), $Na_2[Mo_2O_4(C_{10}H_{12}N_2O_8)]\cdot 1H_2O$; Mo(VI), $Na_4[Mo_2O_6(C_{10}H_{12}N_2O_8)]\cdot 8H_2O$.

with frequencies of 1610 cm.$^{-1}$ or less are considered to be ionically bonded. Conversely, Morris and Busch[3] observed that Co(III)–EDTA, which is considered to be covalently bonded, has an absorption maximum at 1650 cm.$^{-1}$. Thus an increase in the absorption frequency for the COO^- group corresponds to an increase in the covalent character of the metal–carboxylate bond; chelates

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(13) E. S. Gould, "Inorganic Reactions and Structure," Henry Holt and Co., New York, N. Y., 1955, pp. 452.

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

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

TABLE I

INFRARED ABSORPTION PEAKS FOR EDTA CHELATES OF HIGHER VALENT IONS[a]

	r, ionic (covalent)	$—CH_2$	$—COO^-$	$—COO^-$	$—COO^-$		—C—N	$—COO^-$	$—COO^-$	$—COO^-$	
$NaAlY \cdot xH_2O$ $pK = 16.1$	0.45	2940	1570(vs)	1405(vs)	. . .	. . .	1095	. . .	955(s) 935(sh)	845	730
$NaCeY \cdot 2H_2O$ $pK = 16.0$	1.02	2920	1600(vs)	1450(sh) 1415(s)	1340	1260(w)	1100	1030 1000(w)	980(w) 925	855 820	710
$NaBiY \cdot 2H_2O$	1.16	2940	1610(vs) 1570(sh)	1440 1390(s)	1330	1255(w)	1095	1035 1000	980(w) 925	855 830(w)	740 705
$NaVY \cdot 5H_2O$ $pK = 25.9$	. . . (1.22)	2960	1630(vs)	1445(sh) 1405(s)	1330	1280(w) 1250(w)	1115 1080(w)	1040 1000	975 940	880 865 835(w) 810(w)	725
$Na_2VOY \cdot 5H_2O$ $pK = 18.8$	0.64 (1.22)	2960	1630(vs)	1475(w) 1410(sh) 1390(s) 1370(s)	1320	1215	1120(sh) 1095	. . .	970(s) 940(s) 915(sh)	865 835 815	770 715
$NaCrY \cdot 2H_2O$	0.55 (1.17)	2980	1660(sh) 1640(vs)	1470 1440 1360(s)	1315 1290	1240 1160	1090 1075	1040(w) 1015 995	965 930	870 810	750 725
$NaFeY \cdot 1H_2O$ $pK = 25.1$	0.53 (1.17)	2980	1635(vs)	1470 1445 1435 1415 1385(s)	1340 1330	1270	1120(sh) 1105	1030 1010	980 945 930	880 840	745(sh) 720
$NaCoY \cdot 2H_2O$ $pK = 36$	. . . (1.16)	3000	1645(vs)	1475 1440 1385(sh) 1370(s)	1345 1315 1295	1275	1100 1075	1020 1000	975 960 935 915	890 850	755 735 725
$TiOH_2Y \cdot 1H_2O$	0.64 (1.32)	2970	1705 1675 1620(sh)	1475 1465 1440 1405 1370(sh) 1350(s)	1330 1310 1285(s)	1265(s)	1100 1085	1055(w) 1020 995	985 960(sh) 935(s)	870 835	740 715
$ThY \cdot 9H_2O$ $pK = 23.2$	. . .	2920	1630(vs) 1535(sh)	1440 1410(sh) 1395(s)	1340	1285(w) 1255(w)	1120 1105(sh) 1095	1055 1045 1000	985 965 945 930	855 820(w)	740 710
$Na_2Mo_2O_4Y \cdot$- $1H_2O$	. . . (1.29)	2970	1660(sh) 1630(vs)	1450 1400(s) 1385(s)	1355 1340 1300	1240	1110 1090 1065	1045 1005	975 955(sh) 940(s) 910	865 840(w)	760 730(w)
$Na_4Mo_2O_6Y \cdot$- $8H_2O$	. . . (1.29)	2940	1630(vs) 1600(vs)	1475 1455(w) 1420(s) 1395(sh)	1365 1320	1240	1110 1100 1070	1005	985 955 945 900(s)	840(s)	785
$Na_4Y \cdot 0.5H_2O$ $pK = 1.7$	0.98	2800	1605(vs) 1575(sh)	1435 1410(s)	1345(sh) 1325	1285 1260 1190(w)	1145(sh) 1135 1120	1030(w) 1020(w) 1005(w)	990 985 965 925	845	705

[a] Abbreviations used in the table: Y, ethylenediaminetetraacetate; v, very; w, weak; s, strong; sh, shoulder; r, radius, ionic and covalent (the latter are shown in parentheses), ångström units, for the metal ions.[13,14] Frequencies for peaks are given in wave numbers, cm.$^{-1}$. The pK for each chelate (if known)[7-9] is listed below its formula and represents the negative logarithm of the dissociation constant.

with frequencies for this peak of 1630 cm.$^{-1}$ or greater are concluded to be covalently bonded.

Reference to the data in Table I and Fig. 1 indicates that Al(III), Ce(III) and Bi(III) are all bonded ionically to the carboxylate groups of EDTA. In view of the observation for the EDTA chelates of divalent ions that the frequency of the 1600 band generally decreases as the ionic radius increases,[1,2] the low frequency for the Al(III) chelate is surprising. The low frequency might be accounted for if the ionic radius of Al(III) is so small (0.45 Å.) that the metal–carboxylate bond is sterically hindered.

As noted previously,[2] a single sharp peak in this 1600 cm.$^{-1}$ region supports the possibility of a coordination number of six for the metal ion, but it does not prove its existence. The infrared method is particularly effective for indicating that one or more of the carboxylate groups is not bonded to the metal: the presence of an extra peak in the 1600 cm.$^{-1}$ region is strong evidence for a coördination number less than six. This approach has been used effectively in the case of the Co(III)-EDTA chelates[3] and in the case of the Pb(II)-EDTA chelate.[2] The shoulder at 1570 cm.$^{-1}$ for the Bi(III) chelate indicates that one or more of the carboxylate groups of EDTA probably is not bonded to the metal.

The data in Fig. 2 and 3 and in Table I for the 1600 cm.$^{-1}$ peak indicate that V(III), V(IV), Cr(III), Fe(III), Co(III), Ti(IV), Th(IV), Mo(V) and Mo(VI) are bonded covalently to the carboxylate groups of EDTA. The broad bands or shoulders for the COO^- peaks of the V(III), V(IV), Cr(III), Ti(IV), Th(IV) and Mo(VI) chelates may be interpreted in two ways. Either the four carboxylates of the EDTA molecule are bonded to the metal ion in more than one way for these chelates, or one or more of the carboxylates are not bonded to the metal. The latter alternative has been shown by Busch and Bailar[4,6] to be correct for the Pt(II), Pd(II) and Co(III) EDTA chelates and seems reasonable for the Th(IV) chelate; from the spectrum it appears that one of the carboxylates is unbonded to the thorium ion. For the other five chelates either explanation is plausible. The spectrum for the Mo(VI) chelate shows a double peak in the 1600 cm.$^{-1}$ region; apparently two of the carboxylates are bonded to the Mo(VI) ions one way (1630 cm.$^{-1}$ peak) and the other two (1600 cm.$^{-1}$ peak) are either bonded differently or are not bonded to the metal ions at all.

The spectrum for the Ti(IV) chelate in the 1600–1700 cm.$^{-1}$ region shows three peaks (1705, 1675 and 1620 cm.$^{-1}$) which can be attributed to two COOH groups and to two COO^- groups. Both of the COO^- groups may be bonded to the TiO^{++} ion or possibly only one of them. Thus, the infrared spectrum supports the conclusion that the correct formula for the chelate is $TiOH_2EDTA \cdot 1H_2O$ rather than $TiEDTA \cdot 2H_2O$.

The sharp peak for the Fe(III), Co(III) and Mo(V) chelates in the 1600 cm.$^{-1}$ region suggests that all four carboxylate groups of the EDTA molecule are bonded to the metal ion in these chelates. The infrared study of Co(III)-EDTA chelates by Busch and Bailar[4] lends support to this conclusion. Furthermore, for the Co(III) chelate this conclusion is verified by Weakliem and Hoard's X-ray study of the Co(III)-EDTA structure.[16] Their work establishes conclusively that all four carboxylates as well as the two nitrogen atoms of EDTA are bonded to the Co(III) ion.

The symmetrical vibration for the COO^- group gives an absorption band in the 1450–1350 cm.$^{-1}$ region. Because of the multiplicity of peaks, this band is less useful for studying bond character than the antisymmetrical band at 1600 cm.$^{-1}$. However, the 1450–1300 cm.$^{-1}$ band is useful for identification and some correlations are possible between bonding and peak frequency. The spectra for the three chelates in Fig. 1 show no particular trends for this bond, although the Ce(III) and Bi(III) chelates follow the previously noted[1] trend of decreasing frequency for the major peak with increasing ionic radius. The Al(III) chelate does not follow this trend which may be due to its small ionic radius. No significant trends are noted for this bond in the spectra shown in Fig. 2 and 3. However, the general observation can be made that the frequency decreases as the bonding becomes more covalent.

An interesting correlation is observed if the difference in frequency is tabulated between the major peak (or peaks) in the 1600 and 1450–1350 cm.$^{-1}$ bands. The major peaks and their differences are listed in Table II; where two pairs of major peaks are present for a chelate, the second one is listed in parentheses. The peaks for sodium acetate are listed for comparison and illustrate a completely ionic COO^- group. The differences in frequencies range from 150 cm.$^{-1}$ for sodium acetate to 280 cm.$^{-1}$ for the Cr(III) chelate. Reference to Table II indicates that the frequency difference increases as the bonding between the metal and the carboxylate groups becomes more covalent. Thus, the Co(III) and Cr(III) chelates, which are considered to be the most covalently bonded, have the largest frequency differences. Apparently the bonding for the Al(III) chelate is almost as ionic as it is for sodium acetate. By using the frequency difference as the criteria for the degree of covalent character for the metal-carboxylate bonds, an arbitrary designation can be made that the bonds are primarily covalent when the difference is 225 cm.$^{-1}$ or more. When the difference is less than 225 cm.$^{-1}$ the bonding is primarily ionic. The data in Table II indicate that the Mo(V) chelate is considerably more covalently bonded than the Mo(VI) chelate. This conclusion suggests that the oxygen atoms of the Mo(VI)-chelate molecule satisfy most of the coördination sphere of the metal ions. The two molybdenum chelates exhibit considerable splitting in this region which aids in their qualitative identification.

TABLE II

FREQUENCY SEPARATION FOR THE MAJOR ANTISYMMETRICAL AND SYMMETRICAL VIBRATIONS OF THE COO^- GROUPS IN THE EDTA CHELATES

Chelate	Antisymm. freq., cm.$^{-1}$	Symm. freq., cm.$^{-1}$	Freq. difference, cm.$^{-1}$
$NaAlY \cdot xH_2O$	1570	1405	165
$NaCeY \cdot 2H_2O$	1600	1415	185
$NaBiY \cdot 2H_2O$	1610 (1570)	1390 (1440)	220 (130)
$NaVY \cdot 5H_2O$	1630	1405	225
$Na_2VOY \cdot 5H_2O$	1630	1390	240
$NaCrY \cdot 2H_2O$	1640	1360	280
$NaFeY \cdot 1H_2O$	1635	1385	250
$NaCoY \cdot 2H_2O$	1645	1370	275
$TiOH_2Y \cdot 1H_2O$	1620	1350	270
$ThY \cdot 9H_2O$	1630 (1535)	1395 (1410)	235 (125)
$Na_2Mo_2O_4Y \cdot 1H_2O$	1660 (1630)	1385 (1400)	275 (230)
$Na_4Mo_2O_6Y \cdot 8H_2O$	1630 (1600)	1395 (1420)	235 (180)
$Na_4Y \cdot O \cdot 5H_2O$	1605 (1575)	1410 (1435)	195 (140)
NaOAc	1580	1430	150

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(16) H. A. Weakliem and J. L. Hoard, THIS JOURNAL, 81, 549 (1959).

Another band due to the COO$^-$ group appears at 1365–1285 cm.$^{-1}$; the Ce(III) and Bi(III) chelates follow the previously noted trend[2] of the frequency decreasing as the stability constant increases. No apparent correlations exist between the absorption frequency and the character of the chelate for the rest of the complexes in Fig. 1, 2 and 3.

Four additional absorption bands which may be due to the COO$^-$ groups are listed in Table I; at 1285–1160, 1055–995, 990–900 and 890–810 cm.$^{-1}$. No significant correlations can be made but the peaks are useful for identification purposes. The band at 1285–1160 cm.$^{-1}$ may be due to the C-N bond rather than to the COO$^-$ group; spectra for ethylenediamine chelates frequently have an absorption band in this region.

The absorption band at 1145–1065 cm.$^{-1}$ has been assigned to the C-N bond in EDTA chelates[1,2,5] and is exhibited by all of the EDTA chelates collected in Table I. For the chelates in Fig. 1 only one peak is exhibited in this region. For the chelates whose spectra are shown in Fig. 2 and 3, several peaks are shown in this region, which appears to be characteristic of covalently bonded chelates. The frequency of the major peak for these covalently bonded chelates appears to decrease as the bonding becomes more covalent. If this conclusion is correct, then the Mo(V) chelate must be highly covalently bonded.

An additional absorption band appears in the 785–705 cm.$^{-1}$ region for all of the EDTA chelates. Although a specific assignment has not been made for this peak, it is useful for qualitative identification. The strong peak at 840 cm.$^{-1}$ for the Mo(VI) chelate has been established to be due to the Mo–O bond.

Conclusion

The general trends of decreasing frequency with increasing ionic radii, which were observed for the EDTA chelates of divalent ions, are confirmed in the spectra of the Ce(III) and Bi(III) chelates. The infrared data for the COO$^-$ absorption peaks support the conclusion that the bonding for the Al(III), Ce(III) and Bi(III) chelates is primarily ionic. Similar data for the V(III), V(IV), Cr(III), Fe(III), Co(III), Ti(IV), Th(IV), Mo(V) and Mo(VI) EDTA chelates lead to the conclusion that for these complexes the bonding is primarily covalent. Thus, a peak for the antisymmetrical vibration of the COO$^-$ group in the 1610–1550 cm.$^{-1}$ region is evidence for ionic bonding; when this peak is in the 1660–1630 region this is evidence for covalent bonding. As this peak increases in frequency it approaches the frequency of the C=O stretching bond (1700 cm.$^{-1}$), which would be expected for purely covalent bonding.

The data for the 1630–1660 cm.$^{-1}$ band indicate (but do not prove) that the EDTA molecule is serving as a sexadentate ligand in the case of the Fe(III), Co(III) and Mo(V) chelates. A like conclusion is possible in the case of the Cr(III), V(III) and V(IV) chelates but the broader maxima suggest that other interpretations are possible. The shoulders in the 1600 cm.$^{-1}$ region for the Bi(III), Th(IV) and Mo(VI) chelates indicate either that one or more of the COO$^-$ groups are not bonded to the metal ion or that these groups are bonded differently. For the Ti(IV) chelate two of the COO$^-$ groups have protons; thus the chelate has the formula $TiOH_2EDTA \cdot H_2O$.

The difference in frequency between the major peak for the symmetrical vibration (1450–1350 cm.$^{-1}$) and the peak for the antisymmetrical vibration (1660–1570 cm.$^{-1}$) of the COO$^-$ group indicates the degree of covalent bonding for the EDTA chelates. The frequency difference increases as the bonding becomes more covalent; for chelates for which the difference is 225 cm.$^{-1}$ or greater the bonding is concluded to be primarily covalent. If the difference is less than 225 cm.$^{-1}$ the bonding is primarily ionic.

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The Effect of Coördination on the Reactivity of Aromatic Ligands. I. Some Reactions of Trichlorotrianilinechromium(III) and Trichlorotripyridinechromium(III)

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An improved method for preparing trichlorotripyridinechromium(III) and a method of preparing trichlorotrianilinechromium(III) were developed. The reactivity of the coördinated pyridine toward typical electrophilic reagents was examined and, for the experimental conditions used, was found to be identical with that of free pyridine. The reactivity of the coördinated aniline toward bromine was also found to be quantitatively the same as that of free aniline. These observations can be explained readily on the basis of Pauling's principle of electroneutrality. Both of the complexes prepared reacted rapidly with methanol to give conducting species.

Although coördination compounds have been used as catalysts for organic reactions for almost a century, there is very little specific information on how the coördination process, *per se*, compares with typical substituent groups in varying the reactivity of a ligand species. The present work was undertaken to provide information of this sort on pyri-

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