TABLE III

ACTIVATION ENERGY AND ORDER OF REACTION FOR THE THERMAL DECOMPOSITION OF THE URANIUM AND THORIUM CHELATES

Reaction	Reaction order	E^*, kcal./mole
$UO_2(Ox)_2 \cdot HOx = UO_2(Ox)_2 + HOx$	1	26 ± 2^a
$[Th(Ox)_4]_2 \cdot HOx = 2Th(Ox)_4 + HOx$	1	42 ± 4^a

[a] Average of two separate thermograms.

(second step) should be much larger than that of the uranium chelate.

The thermograms of the thorium and uranium chelates are given in Fig. 1. While the uranium chelate loses 8-quinolinol in one step, it is apparent that this is a two step process in the thorium chelate. Borrel and Paris[16] also recognized this and proposed that the first step consisted of an intramolecular dehydration, resulting in the formation of $Th(C_9H_6NO)_4 \cdot (C_9H_6NO)_2O$ and H_2O. Further heating resulted in the volatilization of $(C_9H_6NO)_2O$, leaving $Th(C_9H_6NO)_4$. However, on this basis, the weight loss for the dehydration reaction would be 0.96%; for the second step, it would be 16.18%.

The data in Table IV are in disagreement with this type of decomposition mechanism. There is better agreement with the data if the thorium chelate decomposes thermally according to the reactions

$$2Th(C_9H_6NO)_4 \cdot C_9H_6NOH = [Th(C_9H_6NO)_4]_2 \cdot C_9H_6NOH + C_9H_6NOH \quad (1)$$

$$[Th(C_9H_6NO)_4]_2 \cdot C_9H_6NOH = 2Th(C_9H_6NO)_4 + C_9H_6NOH \quad (2)$$

TABLE IV

WEIGHT LOSS DATA FOR THE THORIUM 8-QUINOLINOL CHELATES

Run no.	Eq. 1, % (from 55 to 185°) Found	Theor.	Eq. 2, % (from 185 to 25) Found	Theor.
436	7.64	7.77	8.64	8.42
435	7.21		8.57	
437	7.71		8.36	
428	6.90		8.52	
431	6.43		8.30	

Discussion

From the magnitude of the heats of solvation, the 8-quinolinol is thought to be held in the crystal lattice by weak electrostatic forces. The values found for the thorium and uranium chelates are larger than the 1 kcal./mole estimated for the scandium chelate.[6]

Since the structures of the metal chelates are unknown, it is difficult to understand the exact nature of the bonding in the crystal lattice. If a layer structure is assumed, bonding similar to that found for chloroform in the chloroform bearing chromium, iron and aluminum acetylacetonates[17] might be expected. The chloroform interaction energy in the metal chelates is about 6.5 kcal./mole of chloroform, a value very similar to that found for 8-quinolinol in this investigation.

Acknowledgment.—The financial assistance of a grant from the Research Corporation is gratefully acknowledged.

LUBBOCK, TEXAS

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(16) M. Borrel and R. Paris, *Anal. Chim. Acta*, **4**, 267 (1950).

(17) J. F. Steinback and J. H. Burns, THIS JOURNAL, **80**, 1839 (1958).

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL SCIENCES, UNIVERSITY OF CALIFORNIA, RIVERSIDE]

Properties and Infrared Spectra of Ethylenediaminetetraacetic Acid Complexes. II. Chelates of Divalent Ions[1]

BY DONALD T. SAWYER AND PAUL J. PAULSEN

RECEIVED JULY 30, 1958

Infrared spectra have been recorded for the EDTA chelates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II). The data, when related to other studies, indicate that the bonding between ligand and metal ion is primarily ionic. Correlations are made between the various functional groups and their resulting absorption peaks. The sodium salts for this group of chelates have been synthesized and isolated.

The chelates formed between the ions of the alkaline earths and ethylenediaminetetraacetic acid (hereafter referred to as EDTA) have been discussed in relation to their infrared spectra in the previous paper of this series.[2] Because EDTA also forms stable complexes with other divalent metal ions, the study of their infrared spectra is of interest and has led to an investigation of the EDTA chelates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II). Although the solution properties of these chelates have been extensively studied,[3-5] little is known of their properties in the solid phase. Also, the type of bonding between the metal ion and the ligand has not been established.

The bonding between the above ions and the ligand would be expected to be primarily ionic,[6] but data are not available to confirm this supposition. The use of the infrared technique to determine whether the bonding in EDTA chelates is ionic or covalent has been reviewed previously.[2] As the

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(1) This research was supported by a grant-in-aid from the Research Corporation. Presented before the Analytical Division of the American Chemical Society in Chicago, Illinois, September, 1958.

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

(3) R. W. Schmid and C. N. Reilley, *ibid.*, **78**, 5513 (1956).

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

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

(6) J. C. Bailar, Jr., "The Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, p. 217–218.

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. The degree of covalent character for the N–metal bond has been shown to be related to the frequency for the band due to the C–N group; the frequency increases as the bond becomes more covalent. Some limitation can be given for the maximum value of the coördination number from infrared data, but the actual value normally 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[7] 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 (purchased from Matheson, Coleman, and Bell) was used in preparing the solid complexes. *p*H titrations indicated that this material was essentially pure and in the form of the dihydrate. The preparation of tetrasodium-EDTA and tetrapotassium-EDTA has been discussed previously.[2] All other materials were reagent grade.

Preparation of Disodium Salts of the EDTA Complexes of Divalent Ions.—The following inorganic salts were used in preparing solid chelates: $\mathrm{MnCl_2\cdot 4H_2O}$, $\mathrm{CoCl_2\cdot 6H_2O}$, $\mathrm{NiCl_2\cdot 6H_2O}$, $\mathrm{CuCl_2\cdot 2H_2O}$, $\mathrm{ZnCl_2}$, $\mathrm{CdCl_2}$, $\mathrm{HgCl_2}$ and $\mathrm{Pb(NO_3)_2}$. To a solution of 0.062 mole of the inorganic salt in 50 ml. was added 0.062 mole of disodium dihydrogen ethylenediaminetetraacetate ($\mathrm{Na_2H_2EDTA\cdot 2H_2O}$) dissolved in 100 ml. of $\mathrm{H_2O}$. The two hydrogen ions released from the ligand were neutralized by adding 0.124 mole of $\mathrm{NaHCO_3}$ to the solution. The resulting solution was adjusted to *p*H 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. The resulting crystalline material was filtered and recrystallized from a water–ethanol mixture. The recrystallized complexes were immediately placed in a vacuum desiccator for 72 hr.

1. **$\mathrm{Na_2[Mn(C_{10}H_{12}N_2O_8)]\cdot 2H_2O}$.**—The complex was analyzed for manganese by precipitating as the pyrophosphate after combustion of the chelate at 900°. *Anal.* Calcd. for complex: C, 28.25; H, 3.79; Mn, 12.92. Found: C, 28.49; H, 4.16; Mn, 11.53.

2. **$\mathrm{Na_2[Co(C_{10}H_{12}N_2O_8)]\cdot 1.5H_2O}$.**—The complex was analyzed for cobalt by electrolysis after combustion of the chelate at 900°. *Anal.* Calcd. for complex: C, 28.59; H, 3.60; Co, 14.03. Found: C, 29.23; H, 4.25; Co, 13.66.

3. **$\mathrm{Na_2[Ni(C_{10}H_{12}N_2O_8)]\cdot 4H_2O}$.**—The complex was analyzed for nickel by electrolysis after combustion at 900°. *Anal.* Calcd. for complex: C, 25.83; H, 4.33; Ni, 12.63. Found: C, 26.30; H, 4.33; Ni, 12.63.

4. **$\mathrm{Na_2[Cu(C_{10}H_{12}N_2O_8)]\cdot 1.5H_2O}$.**—The complex was analyzed for copper by electrolysis after combustion at 900°. *Anal.* Calcd. for complex: C, 28.28; H, 3.56; Cu, 14.96. Found: C, 29.10; H, 3.90; Cu, 15.65.

5. **$\mathrm{Na_2[Zn(C_{10}H_{12}N_2O_8)]\cdot 3.5H_2O}$.**—The complex was analyzed for zinc by precipitation as the sulfide and ignition to the oxide. The chelate was ignited at 900° prior to precipitation of the zinc sulfide. *Anal.* Calcd. for complex: C, 25.96; H, 4.14; Zn, 14.13. Found: C, 26.08; H, 4.29, Zn, 15.15.

6. **$\mathrm{Na_2[Cd(C_{10}H_{12}N_2O_8)]\cdot 2H_2O}$.**—The complex was analyzed for cadmium by polarography after combustion at 900°. *Anal.* Calcd. for complex: C, 24.89; H, 3.34; Cd, 23.29. Found: C, 25.35; H, 3.51; Cd, 23.30.

7. **$\mathrm{Na_2[Hg(C_{10}H_{12}N_2O_8)]\cdot 2.5H_2O}$.**—The complex was not analyzed successfully for mercury. Polarographic analysis indicated that the mercury content was the proper order of magnitude. *Anal.* Calcd. for complex: C, 20.71; H, 2.95. Found: C, 20.81; H, 3.08.

8. **$\mathrm{Na_2[Pb(C_{10}H_{12}N_2O_8)]\cdot 1H_2O}$.**—The complex was analyzed for lead by electrolysis to $\mathrm{PbO_2}$. The chelate was ignited at 900° prior to electrolysis. *Anal.* Calcd. for complex: C, 21.47; H, 2.52; Pb, 37.04. Found: C, 21.11; H, 3.14; Pb, 37.95.

Results and Discussion

The infrared spectra for the EDTA chelates of Mn(II), Co(II), Ni(II) and Cu(II) are shown in Fig. 1. Because these four ions all have unfilled d-subshells, comparison of their spectra as a group

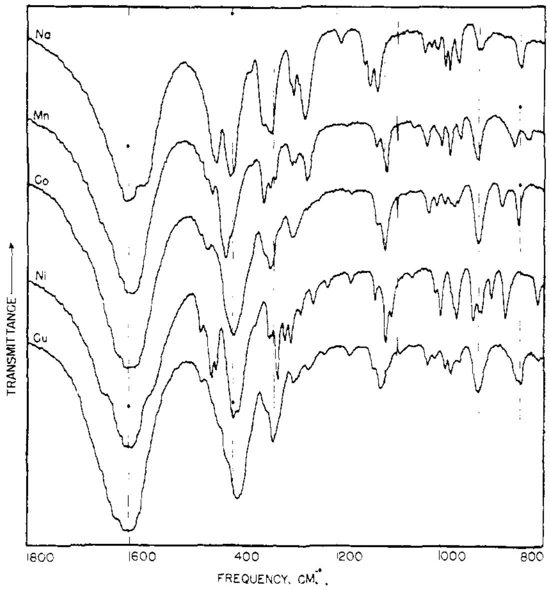

Fig. 1.—Infrared spectra of the EDTA chelates of Mn(II), Co(II), Ni(II) and Cu(II) and of the tetrasodium salt of EDTA: **Na**, $\mathrm{Na_4(C_{10}H_{12}N_2O_8)\cdot 0.5H_2O}$; **Mn**, $\mathrm{Na_2[Mn(C_{10}H_{12}N_2O_8)]\cdot 2H_2O}$; **Co**, $\mathrm{Na_2[Co(C_{10}H_{12}N_2O_8)]\cdot 1.5H_2O}$; **Ni**, $\mathrm{Na_2[Ni(C_{10}H_{12}N_2O_8)]\cdot 4H_2O}$; **Cu**, $\mathrm{Na_2[Cu(C_{10}H_{12}N_2O_8)]\cdot 1.5H_2O}$.

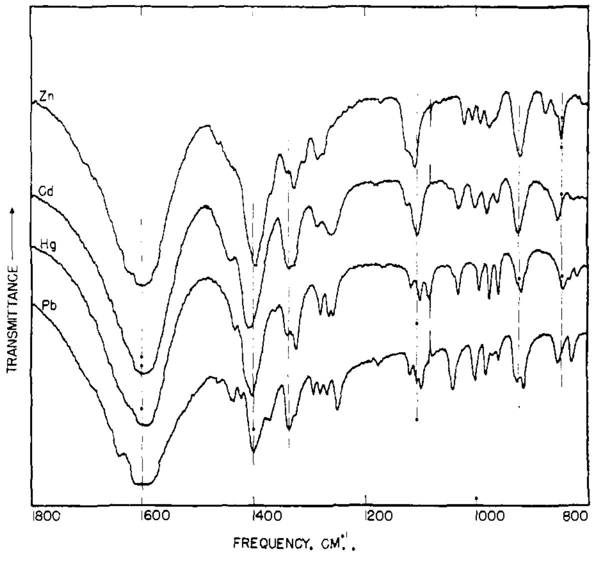

Fig. 2.—Infrared spectra of the EDTA chelates of Zn(II), Cd(II), Hg(II) and Pb(II): **Zn**, $\mathrm{Na_2[Zn(C_{10}H_{12}N_2O_8)]\cdot 3.5H_2O}$; **Cd**, $\mathrm{Na_2[Cd(C_{10}H_{12}N_2O_8)]\cdot 2H_2O}$; **Hg**, $\mathrm{Na_2[Hg(C_{10}H_{12}N_2O_8)]\cdot 2.5H_2O}$; **Pb**, $\mathrm{Na_2[Pb(C_{10}H_{12}N_2O_8]\cdot H_2O}$.

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(7) M. M. Stimson and N. J. O'Donnell, This Journal, **74**, 1805 (1952).

TABLE I

INFRARED ABSORPTION PEAKS FOR EDTA CHELATES AND ACETATES OF DIVALENT IONS[a]

	r, ionic radius	$-CH_2$	$-COO^-$	$-COO^-$	$-COO^-$		$-C-N$	$-COO^-$	$-COO^-$	$-COO^-$
$Na_2MnY \cdot 2H_2O$ $pK = 13.8$	0.80	2920	1600(vs)	1420(s)	1345 1330(sh) 1320(sh)	1290(w) 1280(w) 1260	1125(w) 1105	1025 1000	980 960(w) 930	855 830(w)
$Na_2CoY \cdot 1.5H_2O$ $pK = 16.3$	.78	2950	1600(vs)	1395(s)	1330	1285	1125(w) 1110	1025 1005(w)	970(w) 925(s)	880 850
$Na_2NiY \cdot 4H_2O$ $pK = 18.6$	.68	2950	1605(vs)	1445 1435(sh) 1400(s) 1390(sh)	1330(w) 1315	1300(w) 1290(w) 1270(w) 1245(w)	1130(w) 1105 1095(sh)	1010(w) 1000	970 940 925 905(w)	880 815(w)
$Na_2CuY \cdot 1.5H_2O$ $pK = 18.8$	.69	2930	1605(vs)	1390(s)	1325	1285(w) 1255(w)	1130(sh) 1120	1025(w)	990(w) 980(w) 930(s)	845
$Na_2ZnY \cdot 3.5H_2O$ $pK = 16.5$	.70	2950	1600(vs)	1395(s)	1345(sh) 1330 1310(sh)	1285	1125(sh) 1110	1025(w) 1010(w)	995(w) 980(w) 925(s)	875(w) 850
$Na_2CdY \cdot 2H_2O$ $pK = 16.5$	.92	2920	1595(vs)	1410(s)	1340	1285 1260	1125(sh) 1105	1035 1005	980 965(w) 925(s)	855
$Na_2HgY \cdot 2.5H_2O$ $pK = 21.8$	1.05	2920	1595(vs)	1405(s)	1340(w) 1325	1280 1265 1260	1120(w) 1105(w) 1085(w)	1035	995 980 960 920	845 820(w)
$Na_2PbY \cdot H_2O$ $pK = 18.0$	1.17	2900 2850	1645(sh) 1600(vs)	1440(w) 1400(s) 1375(sh)	1340	1295(w) 1280(w) 1270(w) 1250	1120(w) 1110(w) 1100(w)	1040 1000	980 960(w) 925(s) 915(s)	855 830
$Na_4Y \cdot 0.5H_2O$	0.98	2800	1605(vs) 1575(sh)	1435 1410(s)	1345(sh) 1325	1285 1260	1135 1120	1030(w)	990 985 965 925	845(w)
$K_4Y \cdot$	1.33	2800	1595(vs)	1405(s)	1330	1285 1260	1130 1120	1030(w)	990(w) 980(w) 965(w) 920	845(w)
$Co(OAc)_2 \cdot 4H_2O$	..	......	1705 1560(vs)	1450(s) 1425(s) 1400(s)	1335(s)	.....	......	1025(s)	885	....
$Ni(OAc)_2 \cdot 4H_2O$	..	......	1545(vs)	1425(s)	1350(w)	.....	......	1060(w) 1030	965 910	....
$Cu(OAc)_2 \cdot H_2O$	..	2950(vw)	1620(vs) 1605(vs)	1450(s) 1410(sh)	1355(w)	.....	......	1050(w) 1035(w)	....	....
$Pb(OAc)_2 \cdot 3H_2O$	..	3020(vw) 2980(vw) 2940(vw)	1565(s) 1540(vs)	1415(vs)	1340	.....	......	1045(w) 1015	935	....

[a] Abbreviations used in the table: Y, ethylenediaminetetraacetate; v, very; w, weak; s, strong; sh, shoulder; r, ionic radius, ångström units, for the metal ions.[8,9] Frequencies for peaks are given in wave numbers, cm.$^{-1}$. The pK for each chelate is listed below its formula[10] and represents the negative logarithm of the dissociation constant.

is of interest. For reference, the infrared spectrum for the tetrasodium salt of EDTA is shown at the top of Fig. 1. Guide lines have been placed to aid in comparing the spectra and the major absorption bands. The spectra for the EDTA chelates of Zn(II), Cd(II), Hg(II) and Pb(II) are shown in Fig. 2 and illustrate the infrared characteristics for ions with a filled d-subshell.

In Table I assignments and wave numbers are listed for the major absorption peaks of the eight metal–EDTA chelates. For comparison, similar data are given for the acetates of Co(II), Ni(II), Cu(II) and Pb(II); and also for tetrasodium-EDTA and tetrapotassium-EDTA.

The band at 2800–3000 cm.$^{-1}$ is assigned to C–H stretching in the CH_2 groups of the EDTA molecule.[11] Appearance of this peak in the region of 2900–2950 cm.$^{-1}$ is strong evidence for the formation of a chelate; the acid and the sodium-acid salts of EDTA[2] show this peak at 3020-3030 cm.$^{-1}$ while the trisodium and tetrasodium salts absorb at

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

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

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

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

2800–2810 cm.$^{-1}$. For the acetate salts listed in Table I, the C–H band is extremely weak if observable at all. The characteristic frequency (at 2900 cm.$^{-1}$) for the C–H band in chelated molecules suggests that the COO^- groups of EDTA are directly attached to the metal ion. As seen in Table I, the frequency for the C–H band, in most cases, decreases as the ionic radius increases This also is 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 double peak for Pb(II)–EDTA may be evidence for some difference between the CH_2 groups. This could be accounted for by the presence of one or more carboxylate groups which are unbonded to the lead ion.

Although numerous absorption bands result from the carboxylate group (COO^-) the strongest, and by far the most characteristic, is the band in the 1600-1700 cm.$^{-1}$ region due to C=O stretching. Previous groups[12–15] have discussed the infrared spectra for the carboxylate groups of EDTA, and two groups[2,12] have used the frequency of the C=O group in EDTA chelates as an indication of the covalent character for the metal–carboxylate bond. An increase in the frequency corresponds to an increase in the covalent character; for Co(III)–EDTA,[12] which is considered to be covalently bonded, the frequency for the COOM group is 1650 cm.$^{-1}$. When the frequency for this band approaches 1600 cm.$^{-1}$, the bonding is essentially ionic as illustrated by the data for tetrasodium-EDTA and tetrapotassium-EDTA. Reference to the data in Table I (also Fig. 1 and 2) indicates that all eight of the divalent ions are bonded ionically to the carboxylate groups of EDTA. Although there are no conclusive trends for the 1600 cm.$^{-1}$ peak, the frequency, in general, tends to decrease as the ionic radius increases. The bands for all the chelates are strong, and particularly sharp for Mn(II), Co(II) and Cu(II). The sharpness of this peak has been used to support the assignment of six-coördinate bonding for copper(II)–EDTA[15]; however, reference to Fig. 1 and 2 indicates that all the metal chelates except lead give a fairly sharp peak. This would suggest the possibility that all of these ions are six-coördinate. Such a conclusion is not warranted when it is noted that tetrapotassium-EDTA also gives a single sharp peak at 1595 cm.$^{-1}$. The only justifiable conclusion is that the appearance of a single peak in the 1600 cm.$^{-1}$ region supports the possibility that the metal ion has a coördination number of six; it does not prove it. The 1645 cm.$^{-1}$ shoulder for lead(II)–EDTA is not readily explained but could possibly be attributed to some covalent character for one or two of the metal–carboxylate bonds. An alternate conclusion is that one or more of the carboxylate groups of the EDTA molecule are not bonded to the lead ion. The frequency for the C=O group in lead acetate is distinctly lower than for the lead–EDTA chelate; however, lead acetate also exhibits a double peak.

The rather high frequency for the double peak (1620 cm.$^{-1}$, 1605 cm.$^{-1}$) of copper(II) acetate is surprising and would indicate some covalent character for the metal–carboxylate bond. For the copper(II)–EDTA spectrum the C=O frequency is 1605 cm.$^{-1}$, which is consistent with the other chelates. The transition from a double peak for copper(II) acetate to a single peak for copper(II)–EDTA could be due to the influence of the copper–nitrogen coördination bond in the EDTA chelate. This proposal is supported by the data for the C–N bond which is discussed in a later paragraph.

A characteristic but less useful band, also due to the C=O group, appears in the 1390-1445 cm.$^{-1}$ region. For the chelates shown in Fig. 1 (divalent ions with unfilled d-subshells) the frequency of the major peak decreases as the stability constant increases in magnitude. The decrease in frequency might also be attributed to the filling of the d-subshell. There do not appear to be any significant correlations between this band and the ions in Fig. 2. The Ni(II) and Pb(II) EDTA chelates exhibit considerable splitting for this band and aid in qualitative identification of the specific chelates.

Another band due to the COO^- group appears at 1310-1345 cm.$^{-1}$; for the chelates in Fig. 1 the frequency of the major peak decreases as the stability constant increases. This trend of decreasing frequencies for Mn(II), Co(II), Ni(II) and Cu(II) may also be correlated to the decrease in their ionic radii. The ions in Fig. 2 have a comparable correlation between frequency and stability constant. However, the correlation between ionic radii and frequency ceases to exist. Apparently the frequency for this band decreases as the d-subshell fills; when filled, the frequency shows a discontinuity and no longer exhibits any relationship to the ionic radius. Even the correspondence between frequency and the stability constants is less conclusive for the ions with filled d-subshells.

Four additional absorptions bands which may be due to the COO^- groups are listed in Table I; at 1250-1290 cm.$^{-1}$, 1000-1050 cm.$^{-1}$, 900-990 cm.$^{-1}$ and 810-885 cm.$^{-1}$. No significant correlations can be made, but the peaks are useful for identification purposes. Although not as extensive, the metal acetates also exhibit absorption peaks in all of these regions except the first band at 1260 cm.$^{-1}$. The sequence of peaks is similar for the EDTA chelates but the relative heights and shape are sufficiently different to make these bands quite useful as an aid to qualitative analysis. The band at 1260 cm.$^{-1}$ might be due to the C–N bond rather than to the COO^- group. Infrared spectra for ethylenediamine chelates often have an absorption band in this region.

The absorption band at 1085-1130 cm.$^{-1}$ has been assigned to the C–N bond in EDTA chelates by previous workers[2,15] and is exhibited by all eight metal chelates; the metal acetates do not have a peak in this region. Because there is frequent splitting of the absorption band, several of the resulting peaks can be considered in the study of the bonding for the chelates. By using the peak with the highest frequency in the 1100

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[12] M. L. Morris and D. H. Busch, THIS JOURNAL, **78**, 5178 (1956).

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

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

[15] S. Kirschner, *ibid.*, **78**, 2372 (1956).

cm.$^{-1}$ region, there is a general correlation between the frequency and the ionic radii for all of the metal ions; as the ionic radius increases, the frequency decreases. Apparently the formation of the chelate ring and its resultant geometry has a direct effect on the C–N bond; the smaller ions cause the frequency to be higher. However, reference to Table I and the data for the tetrasodium salt of EDTA indicates that sodium ion does not follow the correlation observed for the other metal ions. Although its ionic radius is greater than that for Cd(II), the frequency for the corresponding peak is some 10 cm.$^{-1}$ higher. This inconsistent characteristic probably can be attributed to the absence of chelate rings in the sodium salt. The frequencies for the two peaks exhibited by the sodium salt should represent the C–N bond in the absence of chelate effects. The absence of significant differences in frequency between the tetrapotassium and tetrasodium salts confirms this supposition, especially in view of the marked difference in ionic radii for the two ions. For the metal chelates the shift to higher frequencies probably can be related to an increase in the strength of the N–metal bond. Smaller ionic radii would appear to favor formation of this bond and could account for the higher frequencies observed for Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Conclusion

The general trends of decreasing frequency with increasing ionic radii, which were observed for the alkaline earth chelates, are confirmed in the spectra for the eight metal chelates considered. The infrared data, especially for the carboxylate groups, support the conclusion that the bonding for the eight metal-chelates is primarily ionic. A carboxylate peak (C=O stretch) in the 1550–1610 cm.$^{-1}$ region is evidence for ionic bonding; other workers[12–14] have evidence for covalent bonding when this peak is at 1625–1650 cm.$^{-1}$. As noted previously,[2] a single sharp peak in this region supports the possibility of a coördination number of six for the divalent metal ions, but it does not prove its existence. The infrared method would be particularly effective in demonstrating that one or more of the carboxylate groups of EDTA is not bonded to the metal. Morris and Busch[12] have used this approach with particular effectiveness for the covalently bonded Co(III)–EDTA chelates. The presence of an extra peak in the 1600 cm.$^{-1}$ region is strong evidence for a coördination number other than six.

The data for Pb(II)–EDTA indicate that there is a difference between the four carboxylate groups (COO^-) in the chelate molecule. This could be accounted for if one or more of these groups were covalently bonded to the lead ion. However, the double peak for the CH_2 band (2900 cm.$^{-1}$, 2850 cm.$^{-1}$) would lend support to the alternate conclusion that one or more of the COO^- groups are unbonded to the lead ion. The latter conclusion would mean that Pb(II) has a coördination number of less than six in the EDTA chelate.

The similarity of all the infrared spectra in Fig. 1 and 2 would also support the conclusion that the bonding for these chelates is primarily ionic. Work in progress on higher valent metal ions indicates that the infrared spectra become more unique as the bonding increases in covalent character. The results of these investigations will be reported in the future.

RIVERSIDE, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CONNECTICUT]

Substitution in the Octahedrally Coördinated Cation Positions in Compounds of the Perovskite Type[1,2]

BY FRANCIS GALASSO, LEWIS KATZ AND ROLAND WARD

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Several phases with perovskite-type structures corresponding to the general formula $A^{II}(B_x^{II}B_y^{III}B_z^{V})O_3$ have been prepared where A^{II} = Ba, Sr; B^{II} = Sr, Ca, Zn, Fe, Co, Ni; B^{III} = Co, Fe; and B^{V} = Ta or Nb. A series of similar phases $A^{II}(Fe_{1-x}^{III}B_x^{V})O_{2.5+x}$ has also been made where x ranges from 0 to $^1/_2$. Other oxygen deficient phases include ordered compounds of the type $A^{II}(B_{1/2}^{II}B_{1/2}^{V})O_{2.75}$ where A^{II} and B^{II} are both alkaline earth ions. From X-ray powder patterns, the following phases appear to be of the cubic perovskite type with cell edges around 4 Å.: $Ba(Fe_{1/2}Ta_{1/2})O_3$; $Ba(Fe_{1/2}Nb_{1/2})O_3$; $Sr(Co_{1/7}^{II}Co_{2/7}^{III}Ta_{4/7})O_3$; $Ba(Zn_{1/3}Nb_{2/3})O_3$; $Ba(Zn_{1/5}Fe_{1/5}^{III}Nb_{3/5})O_3$; $Sr(Zn_{1/3}Ta_{2/3})O_3$; $Ba(Co_{1/3}Nb_{2/3})O_3$. $Ba(Ba_{1/2}Nb_{1/2})O_{2.75}$ and $Sr(Sr_{1/2}Nb_{1/2})O_{2.75}$ are typical of ordered, oxygen deficient phases which require a doubling of the 4 Å. unit cell edge but retain cubic cell shape. For some of the $Sr^{II}(B_{1/3}Ta_{2/3})O_3$ compounds, the powder patterns appear to require a tripling of the 4 Å. unit cell edge. A number of other perovskite-like phases were prepared which gave rather more complex powder patterns; these patterns could, however, be related to a small cubic pseudocell for comparison.

Introduction

The perovskite structure has been found to lend itself to wide departures in composition from the ideal formula ABO_3. Variation may be achieved by isomorphous substitution of either the A or B cations, by valence compensation and by cationic and anionic deficiencies. In many instances, composition changes are accompanied by structural variations, both of which may have profound effects upon the electrical and magnetic properties of the crystals.

Numerous phases typified by the formulas $(BaK)(TiNb)O_6$ and $Ba_3(NiTa_2)O_9$ having the

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[2] Part of this work was abstracted from the Master's Thesis of Francis Galasso, University of Connecticut, 1957.