

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN 53706**Zirconium(IV) and Hafnium(IV) Complexes of α -Hydroxy Carboxylates, Lactates, Mandelates, and Isopropylmandelates. Stereospecificity in Eight-Coordinate Complexes¹**

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The infrared spectra of deuterated (d_4) and protonated tetrakis(*dl*-mandelato)zirconium(IV) and -hafnium(IV) are indicative of a structure containing considerable hydrogen bonding. The neutral stoichiometric tetrakis product from aqueous solution is obtained only with the racemic ligand, suggesting that *dl* ligand pairs provide a stereospecificity suitable for the formation of stabilizing hydrogen bonds which ligands of one handedness do not provide. A polymeric structure possessing bridging ligand pairs between metal ions is proposed. In acetonitrile, mandelic acid reacts with zirconium tetrachloride by anion replacement, to yield a mixture of monochlorotris(mandelato)zirconium and tetrakis(*dl*-mandelato)zirconium(IV) with an infrared spectrum different from that of the aqueous polymeric product.

Introduction

There are a growing number of examples of transition metal complexes in which intramolecular ligand-ligand interactions result in the preferential production of an optically active species.² One often cited example of this phenomenon is the tris(1,2-propylenediamine)-cobalt(III) ion, which is dextrorotatory at the sodium D line when the propylenediamine is levorotatory, but levorotatory when the ligand is dextrorotatory. Sargeson³ describes several other interesting examples, both of the production of complexes with a certain handedness and of preferential coordination by optically active ligands or ligands which become optically active. The nature of the ligand conformations in such coordination number six species was first examined by Corey and Bailar⁴ and refined by others.⁵⁻⁷

Considerable thought^{8,9} has gone into the nature of the coordination polyhedra suitable for species of higher coordination number and the dimensional restraints of the ligand bite, but little attention has been given to the stereospecific effects of ligands. It is of interest, therefore, to look for stereospecific effects of optically active ligands in potential coordination number eight complexes. There are many reports in the literature^{10,11} of complexation of zirconium (hafnium) by polyhydroxy carboxylic acids, polycarboxylates, polyhydroxy alcohols, and other molecules possessing polyfunctional groups, many of which are dissymmetric. Of these mandelic acid was chosen, since tetrakis(*dl*-mandelato)zirconium(IV) seemed to be one of the better characterized compounds.

Experimental Section

Reagents.—Zirconium oxychloride octahydrate was repeatedly

recrystallized¹² until a pure white product was obtained. Hafnium oxychloride octahydrate, free of zirconium, was prepared from hafnium sources available in this laboratory. Pure zirconium tetrachloride was prepared by sublimation of the crude hafnium-free product at least three times. The analytical data agreed well with the theoretical composition for $ZrCl_4$. *Anal.* Calcd: Zr, 39.14. Found: Zr, 39.17, 39.14.

Matheson Coleman and Bell racemic mandelic acid was dried at 50–60° *in vacuo* or sublimed at 110° through a dynamic vacuum. Racemic *p*-isopropylmandelic acid from Eastman Kodak Co., Fisher Analytical Grade 89.6% lactic acid and Aldrich *d*- and *l*-mandelic acid were used as supplied. The optical purity of the *d*- and *l*-mandelic acids was $[\alpha]_D = -149.0 \pm 1.0$ and $+148.0 \pm 1.0^\circ$ compared to the literature values of -154.4 and $+155.5^\circ$.¹³ Deuterated mandelic acid, $C_6H_5CHODCO_2D$, was prepared by equilibrating 0.20 g of mandelic acid with 20 ml of deuterium oxide (40°). At least three equilibrations were required to obtain material in which about 80% of the alcoholic protons were replaced with deuterium (*via* infrared). Free deuterium oxide was removed under vacuum, and the samples were stored in closed containers to prevent exchange with atmospheric water.

Acetonitrile was dried by a modification of the method of Coetzee.¹⁴ The solvent was distilled into storage bulbs which were then frozen, evacuated and sealed. The solvent was subsequently vacuum distilled into the reaction apparatus.

Spectra.—Infrared spectra were taken as Fluorolube and Nujol mulls on a Beckman IR-10 recording spectrophotometer using sodium chloride or cesium iodide plates. Visible and ultraviolet spectra were recorded on a Cary 14 recording spectrophotometer. Optical rotations were measured on a Cary 60 recording spectrophotometric polarimeter.

Synthetic Methods.—Syntheses from acetonitrile were carried out using the inert atmosphere box and glass reaction apparatus described by McDonald.¹⁵

Tetrakis(*dl*-mandelato)zirconium(IV) and -hafnium(IV). Aqueous Solution.—The procedure used is a modification of Hahn and Weber.¹⁶ In a typical experiment from a dilute metal ion solution, 150 ml of $1.7 \times 10^{-3} M$ mandelic acid was added dropwise to 100 ml of 0.005 *M* metal oxychloride solution which is 5 *M* in hydrochloric acid. The solution was stirred continuously at a temperature of 80–90° during the addition. The microcrystalline precipitate formed while digesting for 18 hr was filtered and washed three times with acetone and then three times with ether. The product (identified as B) was dried at 110°. *Anal.* Calcd for $Zr(C_6H_5CHOHCO_2)_4$: Zr, 13.11; C, 55.24; H, 4.06. Found: Zr, 13.10; C, 55.10; H, 4.07. Calcd for $Hf(C_6H_5CHOHCO_2)_4$: Hf, 22.79; C, 49.08; H, 3.61. Found: Hf, 22.78; C, 49.17; H, 3.56.

(1) Abstracted in part from the thesis of E. H. Homeier submitted to the Graduate School in partial fulfillment of the requirements for the Ph.D. degree. Presented in part before the Division of Inorganic Chemistry at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(2) See, for example, M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Chem.*, **9**, 1476 (1970), and references cited therein.

(3) A. M. Sargeson, *Transition Metal Chem.*, **3**, 303 (1966).

(4) E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

(5) J. R. Gollgoy and C. J. Hawkins, *Inorg. Chem.*, **9**, 576 (1970).

(6) J. R. Gollgoy, C. J. Hawkins, and J. K. Beattie, *ibid.*, **10**, 317 (1971).

(7) L. H. Novak and J. K. Beattie, *ibid.*, **10**, 2326 (1971).

(8) J. L. Hoard and J. V. Silverton, *ibid.*, **2**, 235 (1963).

(9) E. L. Muettterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967).

(10) W. B. Blumenthal, "The Chemical Behavior of Zirconium," Van Nostrand, New York, N. Y., 1958.

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(13) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold, New York, N. Y., 1961, p 75.

(14) J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. P. R. Panmanbhan, *Anal. Chem.*, **34**, 1139 (1962).

(15) G. D. MacDonald, M. Thompson, and E. M. Larsen, *Inorg. Chem.*, **7**, 648 (1968).

(16) R. B. Hahn and L. Weber, *J. Amer. Chem. Soc.*, **77**, 4777 (1955).

Preparations from concentrated metal ion solution (0.1–0.5 *M*) followed the same general procedure. In contrast to the slow precipitation observed in dilute solution, precipitation from concentrated metal ion solutions was instantaneous. *Anal.* Calcd for $Zr(C_6H_5CHOHCO_2)_4$: Zr, 13.11; C, 55.24; H, 4.06. Found: Zr, 13.25; C, 53.01; H, 3.88.

Tetrakis(*dl*-mandelato-*d*)zirconium(IV).—The deuterated complex was prepared by the preceding procedure using deuterated mandelic acid in deuterium oxide. Although the solution was 5 *M* in HCl, the total proton content of the solution was only 10–20% of the hydrogen isotopes present. The deuterated complex can also be made by shaking the previously prepared tetramandellate with D_2O for 24 hr at room temperature.

Attempted Preparation of Tetrakis(*d* or *l*)mandelato)zirconium(IV) from Aqueous Solution.—In a typical experiment 0.769 g (5.06 mmol) of *l*-mandelic acid and 0.354 g (1.1 mmol) of zirconium oxychloride were dissolved in 5 ml of water and 10 ml of 5 *M* hydrochloric acid, respectively. After dropwise addition of one-third of the mandelic acid solution to the warm oxychloride solution, a white solid precipitated. The remainder of the ligand solution was added and the resulting mixture allowed to stand overnight. The product was then filtered, washed three times with acetone and ether, and dried at 110°. *Anal.* Calcd for $Zr(C_6H_5CHOHCO_2)_{2.25}(OH)_{1.75}$: Zr, 20.18; C, 47.82; H, 3.68. Found: Zr, 20.32; C, 47.82; H, 3.88.

With the *d* enantiomer, 0.32 g (1 mmol) of zirconium oxychloride was dissolved in 50 ml of 5 *M* hydrochloric acid and mixed with 0.66 g (4.4 mmol) of *d*-mandelic acid dissolved in 150 ml of water. On evaporation to 30 ml, a trace of precipitate was observed; on standing overnight, the amount of solid present increased. The sample was filtered, washed, and dried as above. *Anal.* Calcd for $Zr(C_6H_5CHOHCO_2)_2(OH)_2 \cdot 1.4(C_6H_5CHOHCO_2-d)$: Zr, 14.24; C, 50.94; H, 4.29. Found: Zr, 14.30; C, 51.00; H, 4.06.

Tetrakis(*dl*-mandelato)zirconium(IV) from Acetonitrile Solution.—In a typical experiment 0.923 g (3.98 mmol) of zirconium tetrachloride and 2.42 g (15.9 mmol) of mandelic acid were loaded into different bulbs of an all glass reaction system. After dissolving the reagents in acetonitrile, the mandelic acid solution was poured into the zirconium tetrachloride solution (total volume 120 ml). After standing at room temperature for 3.5 hr the solution was frozen and then pumped on to remove the hydrogen chloride produced. A trace of white precipitate appeared in the thawed solution. Subsequent warming and degassing of the system for 4 hr at temperatures between 27 and 36° produced no immediate change. A significant quantity of white solid precipitated spontaneously about 12 hr after the last degassing. The supernatant liquid was decanted from the precipitate (**B'**), and dried *in vacuo*. The analytical data on this product corresponded to the tetramandellate. *Anal.* Calcd for $Zr(C_6H_5CHOHCO_2)_4$: Zr, 13.11; C, 55.24; H, 4.06; Cl, 0.00. Found: Zr, 12.96; C, 55.19; H, 4.10; Cl, 0.00. The yield was estimated to be 5% based on the mandelic acid used.

The decanted solution was concentrated further by transfer of the solvent on the vacuum line. Precipitation began after about 5 min although pumping was continued until most of the solvent had been removed. The precipitate was separated from the solution by filtration and the rest of the solvent was pumped off. A white product (**A**) mixed with a yellowish product (**A'**) was isolated. The analytical data for three different preparations correspond to mixtures of a monochlorotrakis(*dl*-mandelato)zirconium(IV) identified as **A'** and a tetrakis(*dl*-mandelato)zirconium(IV) identified as **A** which we believe to be different from **B'**. *Anal.* Calcd for $ZrCl(C_6H_5CHOHCO_2)_3$: Zr, 15.72; Cl, 6.11. Found: (1) Zr, 13.81; Cl, 1.29; Cl/Zr, 0.229; (2) Zr, 11.74; Cl, 2.79; Cl/Zr, 0.610; (3) Zr, 12.01; Cl, 4.35; Cl/Zr, 0.932.

Tetrakis(*dl*-*p*-isopropylmandelato)zirconium(IV).—In this preparation 1.96 g (10.1 mmol) of *p*-isopropylmandelic acid dissolved in 100 ml of acetone was added dropwise to 248 ml of warm (60°) 5 *M* hydrochloric acid containing 2.48 mmol of zirconium oxychloride. A precipitate first appeared after about one-third of the ligand solution had been added (~30 min). The suspension was then digested for 1 hr at 60°. The precipitate was filtered after standing 2 days at room temperature, washed with acetone and ether, and dried at 110°; yield is 1.50 g of a white crystalline solid. *Anal.* Calcd for $Zr(C_9H_7C_6H_4CHOHCO_2)_4$: Zr, 10.56; C, 61.15; H, 6.08. Found: Zr, 10.61; C, 61.94; H, 6.44.

Tetrakis(*dl*-lactato)zirconium(IV).—To 0.998 g (3.10 mmol) of zirconium oxychloride dissolved in 227 ml of 1:3 hydrochloric acid, heated to 80°, was added dropwise 50 ml of 2.0 *M* lactic

acid with constant stirring. No product was observed initially although after reducing the volume to about 180 ml a small amount of solid appeared which was removed by filtration and discarded. Reduction of the volume to 10 ml by evaporation at room temperature resulted in a 50% yield of crystalline product. *Anal.* Calcd for $Zr(CH_3CHOHCO_2)_4$: Zr, 20.38; C, 32.20; H, 4.51. Found: Zr, 20.47; C, 31.59; H, 4.49.

Hydroxytris(lactato)zirconium(IV).—To 3.22 g (10 mmol) of zirconium oxychloride in 100 ml of 5 *M* hydrochloric acid at 80° was added 2 ml of 89.6% lactic acid. The warm solution became cloudy almost immediately. After digestion at 80° for 3 days an additional 75 ml of 5 *M* hydrochloric acid was added. The solid which formed was filtered, washed with acetone and ether, and dried *in vacuo*. *Anal.* Calcd for $Zr(OH)(CH_3CHOHCO_2)_3$: Zr, 24.30; C, 28.79; H, 4.30. Found: Zr, 23.80; C, 27.24; H, 4.10.

The Reaction of Tetrakis(*dl*-mandelato)zirconium(IV) with Bases.—Tetrakis(*dl*-mandelato)zirconium(IV) heated with aqueous hydroxide, diethylamine in acetonitrile, or sodium borohydride, calcium hydride, or lithium hydride in acetonitrile resulted in complete solution of the zirconium complex. No characterizable products were obtained from these solutions.

Discussion

Our observation that tetrakis(*dl*-mandelato)zirconium(IV) is not precipitated from aqueous solutions of metal ion concentration less than 10^{-4} *M* is consistent with its solubility of 7.8×10^{-4} mol/l. in 2 *M* perchloric acid.¹⁷ Instantaneous precipitation from aqueous metal ion solutions 10^{-2} *M* or greater and the slow precipitation from solutions 10^{-3} *M* or less is interesting because of the large difference in rate of precipitation accompanying the relatively small change in metal ion concentration. This observation itself deserves further consideration.

It is well established that metal ion and hydrogen ion concentrations are critical in determining the nature of the solute species.^{18–20}

Polymers such as $M_4(OH)_8^{8+}$ and $M_3(OH)_6^{6+}$ are present in low concentrations at total metal ion concentrations of 10^{-4} *M* even at hydrogen ion concentrations of 1–2 *M* and increase in concentration as the total metal ion concentration increases. Thus our rate observations parallel the polymer–monomer metal ion concentrations, the rate being high from solutions of high polymer concentration and low from solutions of low polymer concentration. This leads to the hypothesis that the polymeric metal cation^{21,22} acts as a template for the formation of a polymeric tetrakis(*dl*-mandelato)zirconium species. Since the general features of the infrared spectra are the same for both the product that precipitated rapidly and that which precipitated slowly, the major structural features of the two products are assumed to be the same. Therefore, in dilute solution, the formation of the polymeric tetrakis(mandelato)zirconium is slow, not only because the metal ion concentration is low but also because the polymeric tetrakis(mandelato)zirconium must be formed directly from monomeric metal ions.

The analytical data show that a pure stoichiometric product is obtained only from dilute metal ion solutions; the product from the concentrated metal ion solution is about 95% tetrakis assuming that the im-

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(19) J. S. Johnson and K. A. Kraus, *ibid.*, **78**, 3937 (1956).

(20) E. M. Larsen and P. Wang, *ibid.*, **76**, 6223 (1954).

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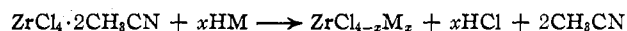
(22) G. A. Muhr and P. A. Vaughn, *J. Chem. Phys.*, **33**, 194 (1960).

purity is a monohydroxytris(mandelato) species. It should be pointed out, then, that if the mandelato species is being used for analytical purposes, the precipitation should be made from solutions of about 10^{-3} M metal ion.

The products obtained from the aqueous solution reaction with the *d* or *l* enantiomer rather than the racemate were either mixtures or hydroxylated products containing less than four mandelate moieties per zirconium. No significance is attached to the formulas calculated from the analytical data, other than the fact that the tetrakis species is not obtained. Thus a stereospecificity of sorts is operative here which requires the presence of ligands which are mirror images rather than ligands of one handedness. A similar situation has been encountered in the case²³ of vanadyl(IV) complexes with various α -hydroxy carboxylic acids where the products with either the *d* or *l* enantiomer alone are not as stable as the product obtained with the racemic acid. Similar phenomena are apparently involved in the copper-tartrate system²⁴ and the cobalt-histadine system.²⁵ However, the zirconium and hafnium tetrakis(mandelates) are the first complexes known that display apparent coordination number eight and stereospecificity.

The physical properties of the tetrakis(mandelate) support the hypothesis that the product precipitated from aqueous solution is polymeric. The very low water solubility of the complex is not surprising in view of its high molecular weight and lack of charge. However, the tetrakis(mandelate) is also insoluble in chloroform, benzene, ethanol, dimethyl sulfoxide, methanol, tetrahydrofuran, diethyl ether, acetonitrile, and methylene carbonate after equilibration for several days at room temperature, in sharp contrast to the solubility of the neutral monomeric tetrakis(2,4-pentanedionato)zirconium(IV) in organic solvents. In addition, the mandelato species does not sublime. Heating to 120–200° at pressures of 10^{-3} Torr results in partial decomposition to mandelic acid, benzaldehyde, an unidentified gas, and a dark solid residue. In contrast, β -diketone derivatives sublime at about 180° under reduced pressure with very little decomposition. Similarly tetrakis(*dl*-isopropylmandelato)zirconium(IV) is also nonvolatile and exhibits very low solubility in organic solvents. The presence of the isopropyl group does not enhance the solubility to nearly the extent as in the case of other metal isopropyltropolonates.²⁶ On the other hand replacement of the phenyl group of the mandelate with a metal group in the lactate gives a tetrakis(*dl*-lactato)zirconium(IV) product which is very soluble and so easily hydrolyzed that previous studies²⁷ had led to the conclusion that a nonhydroxylated species could not be obtained from aqueous solution. It would appear that the phenyl groups of the mandelate shield the zirconium atoms from attack by water molecules.

In acetonitrile the reaction of mandelic acid with zirconium tetrachloride appears to proceed according to the following equation.



Hydrogen chloride is slowly formed in the reaction and is removed by degassing the system on the vacuum line. Hydrogen chloride production is accompanied by the development of a yellow color which is probably due to soluble chloromandelatozirconium(IV) species. After filtering off a small amount of initial product (**B'**), reducing the volume of solution results in the deposition of a mixture of crystalline products, **A** (white) and **A'** (yellow), in varying proportions, depending on the length of time the reaction is run. The analytical data correspond to mixtures of tetrakis(*dl*-mandelato)zirconium(IV), **A**, and chlorotris(mandelato)zirconium(IV), **A'**, with the range 80% **A**–20% **A'** to 80% **A'**–20% **A**. With time or upon attempted recrystallization **A** and **A'** are converted to **B'**.

Structural information of the tetrakis complexes comes solely from an examination of the infrared spectra, since all of the crystals examined by X-rays were twinned. The structurally uninformative phenyl and carbon-hydrogen absorptions have been omitted from the spectra (Figure 1). Stromatt²⁸ reported assignments for the tetrakis(*dl*-mandelato)zirconium(IV), but his conclusions are questionable since he did not consider complications of vibrational coupling which make it impossible to assign most of the absorptions to unique nuclear motions.

There are some absorptions which can be unequivocally assigned to particular vibrations. The asymmetric carbonyl stretching mode which is seen as a strong sharp absorption in the sodium mandelate spectrum at 1620 cm^{-1} and in mandelic acid at 1720 cm^{-1} is replaced by a very broad band in the 1700 to 1500 cm^{-1} range upon formation of the tetrakis species (Figure 1 (1)). This shift is consistent with that observed by Bolard²⁹ for some lactate complexes and with that observed by Kirschner and Kiesling³⁰ in chelated tartrates. The asymmetry of the ν_{as} peak in the spectra of the tetrakis complexes is very striking, especially when compared to the symmetrical peak found in the tris(lactato)hydroxyzirconium(IV) (Figure 1 (5)) and tris(mandelato)lanthanum(III). This asymmetry is consistent with the presence of more than one kind of zirconium-carboxyl bond.

The assignment of the symmetric stretching mode, $\nu_{\text{COO}(\text{sy})}$, is not nearly so clean cut. In the mandelate anion absorption due to this mode is assigned to more than one band because of coupling. In the tetrakis complexes it also seems that several absorptions have $\nu_{\text{COO}(\text{sy})}$ character: the strong absorptions at 1350 cm^{-1} in tetrakis(*dl*-mandelato)zirconium(IV), at 1360 cm^{-1} in the deuterated complex, at 1350 cm^{-1} in the tetralactate, and at 1340 cm^{-1} in the *p*-isopropylmandelato complex. These shifts are apparently due to coupling of skeletal modes. In fact, it is likely that the strong band at 1335 cm^{-1} in the tetrakis(mandelato)metalates and the shoulders at 1345 and 1370 cm^{-1} in the tetrakis(lactato and isopropylmandelato) metalates also have some $\nu_{\text{COO}(\text{sy})}$ character.

The absorption near 370 cm^{-1} is assigned to a zirconium-oxygen motion. However, it is clear from

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(24) N. D. Chasteen and R. L. Belford, *ibid.*, **9**, 169 (1970).

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(29) J. Bolard, *J. Chem. Phys.*, **62**, 887 (1965).

(30) S. Kirschner and R. Kiesling, *J. Amer. Chem. Soc.*, **82**, 1474 (1960).

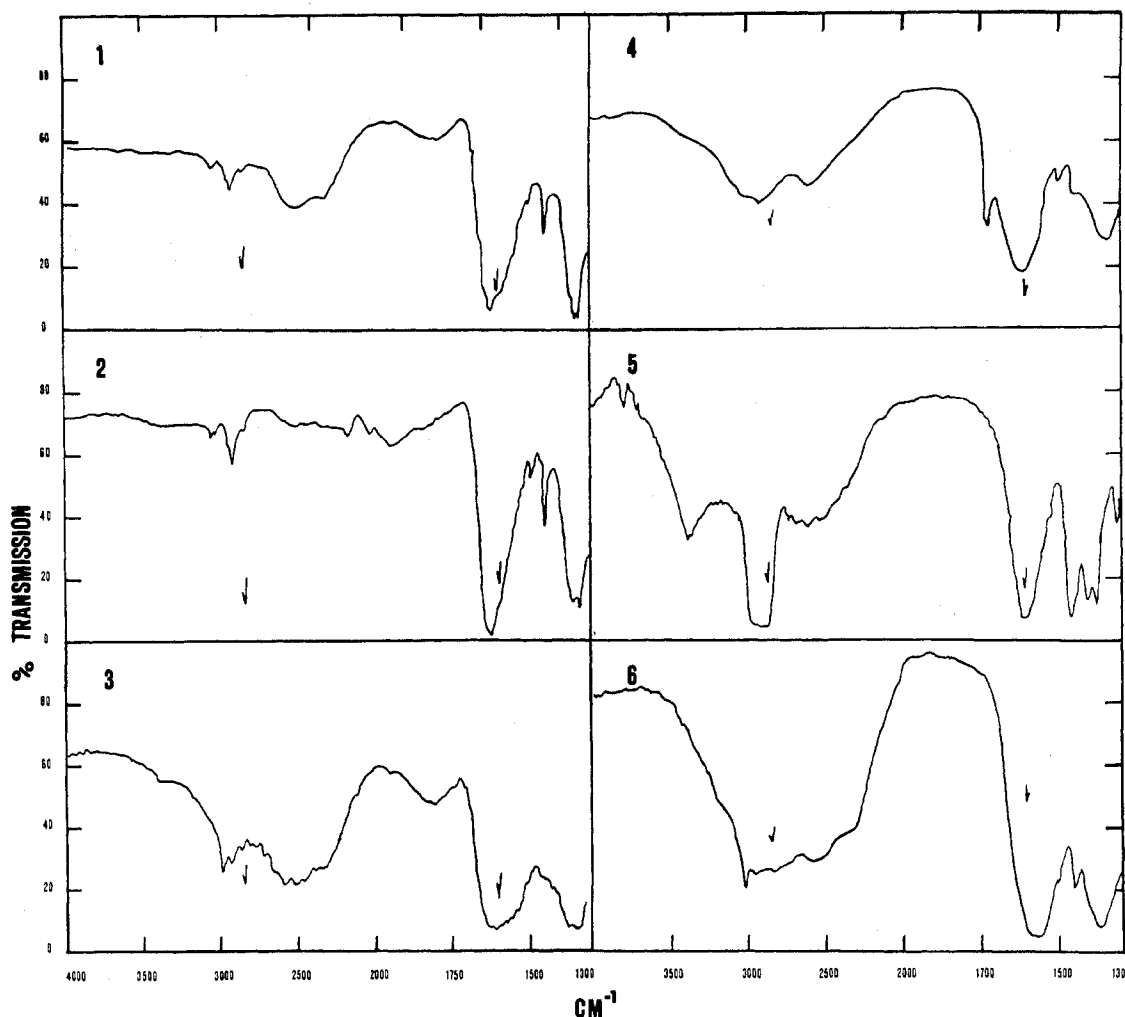


Figure 1.—Infrared spectra of (1) tetrakis(*dl*-mandelato)zirconium, (2) tetrakis(*dl*-mandelato-*d*)zirconium, (3) tetrakis(*dl*-lactato)zirconium, (4) tetrakis(*dl*-mandelato)zirconium (isomer A), (5) hydroxytris(lactato)zirconium, (6) product of *l*-mandelato and zirconium.

examination of the tetrakis(*dl*-isopropylmandelato)-zirconium and tetrakis(*dl*-lactato)zirconium spectra that this band is strongly coupled to other motions, as neither of these complexes have a band at 370 cm^{-1} .

The oxygen-hydrogen stretching regions of the tetrakis(isopropylmandelato, mandelato, and lactato)zirconium spectra are vastly different from those of either the corresponding ligand anion or acid. Instead of a relatively sharp alcoholic ν_{OH} , the tetrakis complexes all show the typical three-band spectrum associated with a harmonic motion of $\text{O}-\text{H}\cdots\text{O}$ in which the oxygen-oxygen distance is near 2.5 \AA . These bands are centered on 2600 (band A), 2300 (band B), and 1850 cm^{-1} (band C), consistent with the observations of many other workers^{31,32} in a wide variety of compounds. There is also a weak absorption near 2700 cm^{-1} which we attribute to a second kind of somewhat longer hydrogen bond ($\text{O}-\text{H}\cdots\text{O}\ 2.7\text{ \AA}$). This appears in the spectrum of the A products (Figure 1(4)) from acetonitrile and the spectrum of hydroxytris(lactato)zirconium (Figure 1(5)) as well. That the A species have more conventional O-H-O distances than the B species is shown by the broad absorptions over the $3200-$

2800-cm^{-1} range. We can conclude that the A species have no double-minimum hydrogen bonds. In addition, the infrared spectrum of the A species shows an absorption at 1700 cm^{-1} which is attributed to an uncoordinated carboxyl moiety and an absorption at 310 cm^{-1} which is assigned to a Zr-Cl mode of the A' chloro complex. This absorption is comparable to the bond at 314 cm^{-1} assigned³³ to the Zr-Cl stretch in chlorozirconium acetylacetonates. Finally the infrared spectra of B and B', and the X-ray powder patterns as well, are identical, showing that the end product from both systems is the same.

The involvement of the alcoholic group in hydrogen bonding is verified by comparison of the spectrum of the tetrakis(*dl*-mandelato)zirconium (Figure 1(1)) with that of the corresponding tetradeuterated complex (Figure 1(2)). The only regions of the spectrum profoundly affected by deuteration are the bands referred to above. New ν_{OD} modes appear as several bands in the $2300-1850\text{-cm}^{-1}$ region. A close comparison of the spectrum of the deuterated species with the spectrum of the protonated species shows that band A is shifted to 2170 cm^{-1} . This is consistent with the observations of Hadzi³¹ and others who have noted that carboxylic acid groups involved in double-

(31) D. Hadzi, "IUPAC VIIIth Symposium on Applied Chemistry, Molecular Spectroscopy," Butterworths, London, 1967, p 435 ff.

(32) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," Benjamin, New York, N. Y., 1968, p 98 ff.

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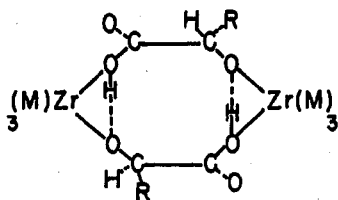


Figure 2.—Schematic drawing of proposed (*dl*-mandelato)zirconium bridged dimer showing the position of the double-minimum hydrogen bonds. M stands for the monomandelato anion, $C_6H_5CHOHCOO^-$.

minimum hydrogen bonds show a shift to a single band at $2155 \pm 25 \text{ cm}^{-1}$ upon deuteration. A comparable shift in band B causes the absorption to overlap the residual low-energy band C. Due to this overlap the fate of C is much more difficult to determine, although there is reason to believe that this absorption shifts to about 1300 cm^{-1} and decreases precipitously in intensity. The weak band at 2700 cm^{-1} , upon deuteration, shifts to 2030 cm^{-1} as expected.

Any proposed structure for the neutral stoichiometric tetrakis(*dl*-mandelato)zirconium must contain the following features: *dl* ligand pairs, short double-minimum hydrogen bonds, a second kind of somewhat longer hydrogen bond, no free carboxyl, alcohol, or metal-bound hydroxyl groups, and carboxyl and alcohol groups which are involved in hydrogen bonding. Among the possible structures is that of discrete molecular units. An examination of Fisher-Taylor-Hirschfelder models using eight-coordinate zirconium(IV) atoms³⁴ shows that it is possible to construct many isomers of discrete eight-coordinate complexes with either dodecahedral or square-antiprismatic geometries. The models also show that carboxyl groups bidentate to a single zirconium or bridging *via* bidentate bonding to two zirconiums are unlikely. The observed hydrogen bonds might be accounted for by invoking intermolecular hydrogen bonds between the discrete molecular species in the fashion found in crystals of copper¹¹ glycolates,³⁵ except that the models show very serious nonbonding interactions between the phenyl rings unless the coordination polyhedron is distorted in a very special way. It also seems that intramolecular hydrogen bonding cannot account for the double-minimum bonds. The average polyhedral edge lengths for other eight-coordinate complexes with oxygen ligands is 2.67 \AA and the minimum edge length not spanned by a chelate group is 2.58 \AA , both distances being too long to accommodate double-minimum hydrogen bonds.

In view of the above, it is reasonable to think of the tetrakis complex as a polymer formed through bridging ligand groups. Examination of models again seems to rule out a polymer formed by preserving the square-plane array found in the aqueous metal ion polymer.^{21,22} In such a species there are prohibitively large nonbonding interactions between groups attached to different metal ions. However, it is conceivable that the tetramer opens up to more or less linear array with three chelated anions on terminal cations and chain links of zirconium moieties bearing two chelated bidentate ligands and two bridging ligands. Complexes with

more than two bridging mandelates per metal atom were eliminated because the more highly cross-linked polymers require the presence of more than four metal atoms to form a contiguous crystalline array. Since the essential features of higher polymers are identical with those of a dimer, the proposed structure (Figure 2) is limited to this species.

In the proposed dimer, *dl* ligand pairs in a bridge between two Zr(IV) atoms are opposed to one another such that short double-minimum hydrogen bonds are formed between the alcoholic proton and the oxygen of the carboxyl group, while somewhat longer hydrogen bonds are formed intramolecularly between the oxygen atoms of the ligands which are bidentate to the same zirconium atom. The stability of the structure depends upon the presence of these hydrogen bonds, which can only be achieved with *dl* pairs and not with pairs of one enantiomer alone. This relationship between stereospecificity and hydrogen bonding has been shown to exist in compounds such as $(+)_495[L\text{-glutamato}(\text{en})_2\text{Co}][\text{ClO}_4]^{36}$ and in $[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$.³⁷ It is apparent from the models that the complexes are less strained if the carboxyl or alcoholic functionality is slightly removed from the coordination sites. Since strain relief would occur, the question of whether the resultant species is really seven- or eight-coordinate is problematic. It should be pointed out again that the asymmetric shape of the $\nu_{\text{COO}(\text{as})}$ absorption may indicate the presence of two kinds of carboxyl-zirconium bonds. The models also confirm that hydrogen bonds of the second type can be formed between oxygen atoms of the terminal chelated ligand molecules. Thus the proposed structure satisfies all the spectral and physical properties of the tetrakis species.

The importance of these hydrogen bonds in tetrakis(*dl*-mandelato)zirconium(IV) is underlined by its reaction with bases in either aqueous or nonaqueous solution. The bases attack the hydrogen-bonding protons either by neutralization or oxidation-reduction, resulting in the complete dissolution of the formerly insoluble product. The solids isolated from these solutions are not characterizable as pure compounds and do not correspond to salts of the Zr(*dl*-mandelate)₄⁴⁻ anion as previously claimed.³⁸ It is concluded that the zirconium atom becomes susceptible to attack by the solvent molecules upon destruction of the hydrogen-bonded structure and that soluble solvated products result.

In contrast to the polymeric eight-coordinate structure of B, the tetrakis(*dl*-mandelato) A species and the chlorotris(*dl*-mandelato) A' species are thought to be seven-coordinate soluble monomers. The relative intensities of the $\nu_{\text{C=O}}$ and $\nu_{\text{COO}(\text{as})}$ bands in the infrared spectrum of A suggest that there is an uncoordinated carboxyl group present. The symmetric shape of the asymmetric carboxyl stretch and the single band in the alcoholic ν_{CO} region appear to show that the other mandelate anions are bidentate. Since no double-minimum hydrogen bonds are present there are no

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bridging mandelate ligands present. The absorption centered on 2600 cm^{-1} can be assigned, as in the case of **B**, to intramolecular hydrogen bonds involving the oxygens of chelated bidentate ligands. Dimerization of the **A** species produces the **B'** species, which is identical with the aqueous **B** product. Thus **A** may be considered an isomer of the aqueous product **B**. This brings us to the question of the nature of the yellow **A'** species. A methanol solution of this product, for which a visible-ultraviolet spectrum was taken, showed a featureless Laporte allowed transition tailing off at about 490 nm and going off scale at 364 nm which is

attributed to chlorozirconium transition. Since the metal-bound chloride is clearly seen in the infrared spectrum and the rest of the spectrum is very similar to that of **A**, the structure of **A'** is envisioned to be the same as **A**, except that the monodentate mandelate is replaced by a chloride.

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Proton Nuclear Magnetic Resonance Studies of Several Polyaminocarboxylic Acid Complexes of Vanadium(V)

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The solution structures and equilibria of the vanadium(V) complexes formed by ethylenediamine-*N,N,N',N'*-tetraacetate (EDTA), ethylenediamine-*N,N'*-diacetate (EDDA), and *N,N'*-dimethylethylenediamine-*N,N'*-diacetate (DMEDDA) have been studied by proton nuclear magnetic resonance spectroscopy. All three complexes have the formula $[\text{VO}_2\text{Y}]$, where Y represents EDTA, EDDA, or DMEDDA, and have been isolated as the sodium or potassium salts. Infrared spectra indicate that the oxygen atoms in the VO_2 unit have a cis conformation. Structures are proposed for all three complexes on the basis of the nmr and infrared data. The EDTA and DMEDDA complexes appear to form a single isomer (α -cis), while the EDDA complex forms both α -cis and β -cis isomers. The β -cis \rightleftharpoons α -cis equilibrium has been studied at several temperatures to evaluate the thermodynamic parameters.

Proton nuclear magnetic resonance (nmr) has proven useful for the study of numerous metal ion complexes with polyaminocarboxylic acids such as ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA).¹⁻⁷ If the metal-ligand bonds are long-lived compared to the nmr time scale, considerable information about the solution structures of these compounds can be obtained. For such conditions the methylenic protons of the acetate group become chemically nonequivalent, due to the asymmetric bonded nitrogen atom, giving rise to an AB spin-spin splitting pattern.¹ From the coupling constant and chemical shift difference between the two protons, the environment of the acetate group and its position relative to the N-metal-N plane can be determined.^{1,3-6}

Vanadium(V) (d^0 electronic configuration) normally forms octahedral complexes.⁸ The solution equilibria of the vanadium(V) complex with EDTA have been studied; the one-to-one complex has a $\log K_{\text{stab}}$ value of 15.55.⁹ The present investigation has been undertaken to study the solution structures of the chelates of vanadium(V) with EDTA, ethylenediamine-*N,N'*-diacetic

acid (EDDA), and *N,N'*-dimethylethylenediamine-*N,N'*-diacetic acid (DMEDDA) by means of proton nmr and infrared spectroscopy.

Experimental Section

The nmr spectra were recorded with a Varian HA-100 high-resolution spectrometer equipped with a variable temperature probe and operating at 100 MHz; the ambient probe temperature was 32°. Varian precision-bore nmr tubes were used for all measurements. Two small drops of reagent-grade *tert*-butyl alcohol were added to each sample to serve as the lock signal and internal reference. Deuterium oxide was used as the solvent. The concentration of complex in each sample was $\sim 0.7 F$. All chemical shift values are referenced to TMS. Peaks were integrated by use of a compensating polar planimeter. Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer, with the samples dispersed in KBr disks.

Measurements of pH were made with a Leeds and Northrup Model 7664 line-operated pH meter equipped with micro electrodes, which were standardized against Leeds and Northrup buffer solutions; data were obtained at 25°.

Disodium ethylenediamine-*N,N,N',N'*-tetraacetate dihydrate and vanadium pentoxide (assay 100.0%) were obtained from J. T. Baker Co., and ethylenediamine-*N,N'*-diacetic acid (assay 98+%) was obtained from Aldrich Chemical Co.; these materials were used without further purification. Deuterium oxide (isotopic purity 99.8%) and reagent grade *tert*-butyl alcohol were supplied by Mallinckrodt Chemical Works.

Ammonium metavanadate was prepared and purified by the method of Baker, *et al.*;¹⁰ its infrared spectrum coincided exactly with that reported by Miller and Wilkins.¹¹ Barium *N,N'*-dimethylethylenediamine-*N,N'*-diacetate was prepared by the method of Legg and Cooke;⁵ no nmr-detectable impurities were

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