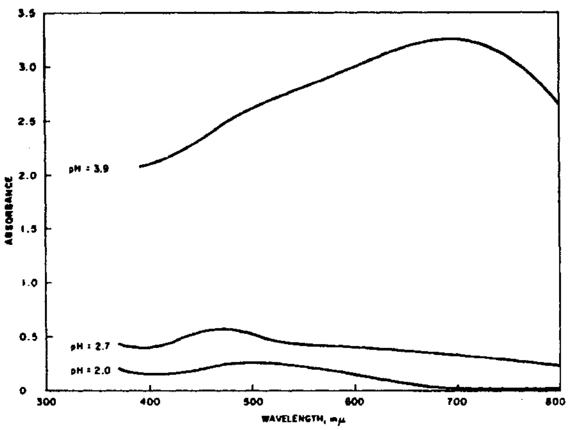

Fig. 2.—Variation of absorbance with pH for 8 mM titanium(III) in 0.75 M KI solution.

pH had remained constant. At pH 3.9, a 10% increase occurred at 800 mμ after only 15 min. From these results, it is concluded that polynuclear species with an absorption maximum near 700 mμ are slowly formed from $Ti(OH)^{+2}$, which has an absorption maximum at 480 mμ. The spectrophotometric evidence also indicates that negligible amounts of polynuclear species were present in the pH region where the log K_1 values were determined for the present work. Since the absorbance of this polynuclear species is so much larger than that of Ti^{+3}, spectrophotometric evidence of its existence is a much more sensitive measurement than the material balance which is reflected by the pH measurements. It also can be concluded from this and the titration shown in Fig. 1 that only negligible amounts of $Ti(OH)_2^+$ exist in these concentration ranges and that a simple $Ti(OH)_3$ is probably formed only by a very rapid addition of base to an acidic titanium(III) solution.

Whenever the pH was allowed to exceed 5, very rapid oxidation of the titanium(III) was found to occur. This presumably is due to the formation of hydrogen through reduction of water by titanium(III).[14]

Acknowledgment.—Special acknowledgment is due to the U. S. Naval Ordnance Test Station, China Lake, California, for granting a leave of absence and two fellowships to A. N. Fletcher.

[14] B. Diethelm and F. Foerster, *Z. physik. Chem.*, **63**, 129 (1908).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Compounds Exhibiting Coördination Number Eight. The Potassium Tetraoxalatometallates of Zirconium(IV), Hafnium(IV), Thorium(IV), and Uranium(IV)[1]

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Received September 27, 1961

The conditions have been studied for the preparation of the tetraoxalatometallates of zirconium(IV), hafnium(IV), thorium(IV), and uranium(IV), free of hydrolysis products. The zirconium and hafnium compounds are monoclinic with four molecules in the unit cell. The crystals belong to the space group $P2_1/a$, which permits the existence of mirror images in the solid state. Attempts to resolve the possible racemic pairs of these anions were unsuccessful. Oxalate exchange studies with C-14 containing oxalic acid showed that complete exchange occurred within a few minutes time of the experiment. It is shown that the anions lose oxalate by hydrolysis and/or aquation. The infrared spectra have frequencies for O–C–O vibrations about half way between those for the oxalate ion and a covalent oxalate molecule.

Introduction

For molecules or ions exhibiting coördination number eight, geometrical and optical isomers are possible, the number depending upon the kinds of groups involved and the geometry of the complex. The number of isomers for all classes of coördination number eight compounds has been calculated by Marchi.[3] For zirconium, hafnium, ura-

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[1] This article is based on a dissertation submitted by F. A. Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. Presented before the Division of Inorganic Chemistry at the 134th National Meeting of the American Chemical Society, Chicago, September, 1958.

[2] National Science Foundation Predoctoral Fellow 1956–58.

[3] L. E. Marchi, W. C. Fernelius, and J. P. McReynolds, *J. Am. Chem. Soc.*, **65**, 329 (1943).

nium, and thorium with oxy-ligands, the antiprismatic arrangement[4-6] and the dodecahedral arrangement[7] have been reported. For a molecule or ion with four symmetrical bidentate ligands with the antiprism arrangement, three different orientations are possible all of which have non-superimposable mirror images and thus would be optically active. If the symmetry of the ligands is dodecahedral, six different arrangements[8] are possible, four of which have non-superimposable mirror images and thus are optically active, and two of which have superimposable mirror images and thus are inactive.

There exists only one report of the partial resolution of such a unit, and that is the tetraoxalatouranate(IV) ion.[9] It was this report which led to this investigation of the preparation and properties of these oxalatoanions. However, our initial observations on the preparation of salts of the tetraoxalato anions gave us some doubts as to whether the separation of optical isomers of these compounds ever had been achieved.

The syntheses of potassium and ammonium tetraoxalatozirconates have been reported by a number of workers;[10-15] however, the procedures are vague and the products have been characterized by analysis only. The solubility of thorium oxalate in excess oxalate has been noted,[16] and is the basis of our synthesis. A procedure for the preparation of potassium tetraoxalatouranate(IV) has been described[9] and was improved upon.

Discussion of Results

The preparation of potassium tetraoxalatouranate(IV) 5-hydrate by Marchi's procedure[17] yielded a product which had an oxalate–uranium ratio of 3.70 rather than 4.00. This agrees with the analytical data in his thesis.[18] It was found that a product of mole ratio 4.00 could be obtained if the original preparation was reprecipitated with alcohol from a nearly saturated solution of the complex to which was added excess potassium oxalate and oxalic acid. In the preparations of all these oxalatoanions the proper product could be obtained only in the pH range established by the potassium oxalate–oxalic acid buffer. The critical oxalate and hydrogen ion concentrations are related to a hydrolysis equilibrium involving the tetraoxalatoanions.

By the same token, when the tetraoxalatometallates are dissolved in water an instantaneous drop in pH is noted. This requires the loss of oxalate from the complex and the production of hydrogen ions, together with aquated and/or hydrolyzed metal species. The following general equation describes the major species in such a solution. The total quantity of oxalate lost by

$$y\,\mathrm{M(Ox)_4}^{-4} + 2y\,\mathrm{H_2O} \longrightarrow (y - z)\,\mathrm{M(Ox)_3(H_2O)_2}^{-2} + z\,\mathrm{M(Ox)_3(H_2O)(OH)}^{-3} + \frac{K_2y}{K_2 + (\mathrm{H}^+)}\,\mathrm{HOx}^{-1} + \frac{(\mathrm{H}^+)y}{K_2 + (\mathrm{H}^+)}\,\mathrm{Ox}^{-2} + \left(z - \frac{K_2y}{K_2 + (\mathrm{H}^+)}\right)\mathrm{H}^+$$

the tetracomplex is y. The oxalate ions Ox^{-2} and HOx^- are related by the observed pH and K_2 of oxalic acid. Since they must sum to y they must have fractional coefficients. In the limit that there is no diaquo (*i.e.*, the least oxalate release which can account for the observed pH), $y = z$ and one can obtain a numerical value for y with which the average oxalate/metal ratio can be calculated. For a 0.01 M solution of the zirconium complex, the observed pH of 4.40 can be accounted for by a concentration of 6.5×10^{-5} M total free oxalate. Hence the average oxalate/metal ratio of the recrystallized complex need change only from 4.000 to 3.994. This is in fact what is found. For the uranium and thorium complexes, 0.01 M solutions had pH values of 4.80 and 6.29, respectively. The uranium product recovered from solution had an oxalate–uranium ratio of 3.76, whereas the thorium complex yielded a soluble and insoluble portion for which the mole ratios were 3.86 and 2.38, respectively. To account for both the observed pH and the decrease in the oxalate/metal ratio of the products recovered from the solution, one must conclude that loss of oxalate by aquation alone for these anions is greatest for

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(4) A. Clearfield and P. A. Vaughan, *Acta Cryst.*, **9**, 555 (1956).

(5) J. V. Silverton and J. L. Hoard, New York Meeting, American Chemical Society, 1960.

(6) D. Grdenić and B. Matković, *Nature*, **182**, 465 (1958).

(7) J. L. Hoard, G. L. Glen, and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 4293 (1961).

(8) An error was found in the isomer count[3] for the dodecahedron with four symmetrical (C_{2v}) bidentate ligands. One of the five pairs of optical isomers given by the authors possesses a four-fold axis of alternating symmetry; hence, there should be listed only four pairs of active and two inactive forms.

(9) L. E. Marchi and J. P. McReynolds, *J. Am. Chem. Soc.*, **65**, 333 (1943).

(10) S. R. Paykul, *Bull. soc. chim. France*, **20**, 65 (1873).

(11) F. Venable and C. Baskerville, *J. Am. Chem. Soc.*, **19**, 12 (1896).

(12) A. Mandl, *Z. anorg. u. allgem. Chem.*, **37**, 252 (1903).

(13) A. Rosenheim and P. Frank, *Ber.*, **38**, 812 (1905); *ibid.*, **40**, 803 (1907).

(14) P. Pfeiffer, *Z. anorg. u. allgem. Chem.*, **105**, 29 (1919).

(15) J. Boulanger, *Compt. rend.*, **202**, 2156 (1936); *ibid.*, **203**, 87 (1936).

(16) P. T. Cleve, *Bull. soc. chim. France*, **21**, 122 (1874).

(17) L. E. Marchi, "Inorganic Syntheses," Vol. III, L. F. Audrieth Editor, McGraw-Hill Book Company, Inc., New York, N. Y., 1950.

(18) L. E. Marchi, Ph.D. Thesis, The Ohio State University, 1943.

thorium and smallest for zirconium and hafnium. Thus hydrolysis is most important in the zirconium and hafnium complexes, and least important in the thorium complex. This trend follows the order of increasing size of the central atom and is consistent with other observations on hydrolysis.

The labile nature of these anions made it seem unlikely that optical isomers would be found. However, X-ray studies on single crystals of the hafnium compound held out some hope for the presence of optically active species. The hafnium and zirconium compounds were found to belong to the monoclinic system. Systematic absences in the 0*k*0 reflections showed that there was a screw axis parallel to "*b*." Systematic absences in the *h*0*l* reflections revealed a glide plane perpendicular to "*b*" with translation *a*/2. The combination of these two symmetry elements allowed determination of the space group as the unique $P2_1/a$. The number of formula weights per unit cell was determined to be four. For this space group the presence of four molecules per unit cell usually means that there are two types of molecules, each kind being the mirror image[19] of the other. Now if the symmetry around the zirconium atom is that of the antiprism, then the mirror images also should be non-superimposable, and hence the ions should be optically active. However, the data[7] on $Na_2Zr(C_2O_4)_4 \cdot 2H_2O$ show that the symmetry around the zirconium is dodecahedral. The isomer count referred to earlier permits in this case two inactive forms as well as four racemic pairs. The point group symmetry established by Hoard requires the presence of a mirror plane in the anion, and thus the anion is in one of the inactive forms. The space group $P2_1/a$ for the compound reported here, $K_4Hf(C_2O_4)_4 \cdot 5H_2O$, requires that no more than two forms of the complex anion can be deposited in the same crystal from aqueous solution. However, the symmetry about the metal was not established. If the assumption is made that the symmetry about the metal in this case is the same as in the sodium salt, and that the symmetry remains the same in solution, then no optical activity would be expected. Since the zirconium and hafnium X-ray data are very much alike, it is evident that the two compounds are isomorphous, and that the same conclusions can be drawn for each.

It seems likely that the thorium and uranium complexes also are monoclinic, but the powder data are not enough to establish the space group and the unit cell dimensions unequivocally. The uranium and thorium compounds appear to be isomorphous but different from the zirconium and hafnium compounds.

This work was completed before Hoard established the dodecahedron as the configuration for the tetraoxalatozirconate anion. At the time, the apparent preference for the antiprismatic arrangement for the eight oxygens about the metal gave some hope that the separation of racemic pairs of anions could be performed. The experimental procedure of Marchi[9] for the attempted resolution of isomers of the tetraoxalatouranate(IV) anion was followed exactly except for the fact that the starting material had a 4:1 oxalate–metal mole ratio. The rotations of materials prepared and examined by the prescribed procedures always were within 0.010° of zero rotation. The results on the products corresponding to the claimed four isomers are summarized in Table I.

TABLE I

	Marchi		This Work	
Isomer	Rotation	Concn., %	Rotation	Concn., %
"Unstable *dextro*"	+0.10°	0.26	−0.001°	1
"Unstable *levo*"	−0.10°	?	−0.002°	1
"Stable *dextro*"	+0.07°	0.47	−0.004°	1.48
"Stable *levo*"	−0.05°	0.05	+0.001°	0.5

It was estimated that if a rotation of 0.020° were considered significant, specific rotations of 0.5°–100 ml./dm./g. or less could have been detected. Since specific rotations of most coordination compounds which have been resolved unequivocally are in the range 10–10,000°, we concluded that there has been little or no resolution of isomers in this case. No mutarotations or racemizations such as previously reported ever were observed.

The negative rotations observed were shown to be due to dissolved strychnine iodide. It was found that when the alkaloid was added to a saturated solution of potassium iodide in the absence of the uranium complex, the filtrate after the removal of the solid alkaloid iodide had a rotation of −0.043°, which corresponded to 0.05 g./l. of strychnine iodide. After removal of strychnine by this method, the rotations of samples containing uranium anion approached this value.

The fact that 4:1 zirconium and hafnium com-

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(19) C. W. Bunn, "Chemical Crystallography," Oxford University Press, New York, N. Y., 1952, p. 249.

plexes could be recovered easily from water solution suggested that these compounds might be less labile than the uranium compound. Therefore resolutions also were attempted with the tetraoxalatozirconate ion. Rotations obtained on fractionally precipitated zirconium tetraoxalate which had been freed of strychnine in no instance exceeded −0.009°, which was not considered significant. The concentration of tetraoxalatozirconate ion in these solutions was about 0.5 g./100 ml. and specific rotations of 5° should have given significant rotations. Fractional crystallization experiments carried out using quinine as the resolving agent gave 0.01 M solutions (freed of quinine) which had rotations of about −0.050°. These rotations are ascribed to the quinine remaining in the solution due to the solubility of quinine iodide. Again we concluded that no resolution was obtained. Owing to the instability of the thorium tetraoxalato anion in water no resolutions were attempted with this compound.

The labile nature of these anions was confirmed by exchange studies with C^{14} containing oxalate. After a solution containing the tetraoxalatometallate anion and tracer had been prepared, a sample was recovered by alcohol precipitation. This procedure was chosen rather than that of precipitation of the complex anion as an insoluble salt because calcium oxalate and uranium oxalate precipitation takes place upon the addition of calcium ions to the tetraoxalatouranate solutions. Hence, the procedures of Long[20] were not applicable here.

Most of the exchanges were performed at different inactive oxalate concentrations to ensure that the small amount of oxalate provided by the radioactive oxalate would not be absorbed on the voluminous precipitate. No such effect was noticed. The data are given in Table II. The values of less than 100% exchange for the zirconium and hafnium compounds are not considered significant. They seem to be related to self-absorption in the hard crystalline precipitates. Whereas the uranium compound precipitated as a fine microcrystalline powder, the zirconium and hafnium compounds came down as hard granular crystals. Even after these were ground to a diameter of about 0.07 mm. the sample preparation was erratic. The data indicate that exchange occurs in all three tetraoxalato anions within the time required for the experiment. Such a rapid oxalate exchange confirms the lability of these anions, and supports the lack of success in the resolution attempts.

TABLE II

Concn., M $K_4M(C_2O_4)_4$	Concn., M $K_2C_2O_4$	Time, Min.	Temp., °C.	% Exchange
		Uranium		
0.242	0.000	7.5	23	100
.193	.144	7.5	23	99
.128	.278	7.5	24	103
.136	.179	2.5	23	105
.0776	.0507	5.0	3	99
		Zirconium		
0.111	0.000	10	25	100
.111	.000	5	23	92
.0630	.000	3	25	110
.0532	.0448	5	25	95
.0137	.0146	10	5	101
		Hafnium		
0.0300	0.000	2.5	25	86
.0270	.000	2	25	89
.0270	.000	600	25	89
.0220	.148	300	65	100
.0220	.076	60	65	101

The infrared spectra over the range 4000–300 cm.$^{-1}$ (Table V) show an interesting similarity to the spectra of the trisoxalato complexes of aluminum, chromium, iron, and cobalt as determined by Quagliano.[21] Above 700 cm.$^{-1}$ the same six major bands show up, although those in the neighborhood of 1600–1700, 1280, and 800 cm.$^{-1}$ are not doublets as they are in the six coördinate case. Quagliano attributed these three groups to B_1 vibrations of the O–C–O group with the doublets due to the coupling of the three oxalate groups. Perhaps the change in symmetry from the C_{2v} of the octahedron to C_{4v} of the antiprism or D_{2d} of the dodecahedron is responsible for the change in spectrum.

At the shorter frequencies, the 480 cm.$^{-1}$ band which is present in the 6-coördinate species also is present in these compounds although it is shifted to slightly higher values. The same is true for the 580 cm.$^{-1}$ band except in the case of thorium, where it seems to be absent. The spectra of the zirconium and hafnium compounds are very similar over the whole range, whereas the uranium and thorium show some differences especially at the lower frequencies.

As with the 6-coördinate species[21] the carboxylate frequencies are between those of the oxalate ion in the alkali metal oxalates and dimethyl oxalate, which is representative of covalent bond-

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[20] F. A. Long, *J. Am. Chem. Soc.*, **63**, 1353 (1941).

[21] M. J. Schmelz, T. Migazawa, S.-I. Mizushima, T. S. Lane, and J. V. Quagliano, *Spectrochim. Acta*, **9**, 5158 (1954).

TABLE III

	% Metal		% Oxalate		Moles	% H_2O	
	Calcd.	Found	Calcd.	Found	C_2O_4/M	Calcd.	Found[a]
U							
5.00 H_2O	28.46	28.67 ± 0.10	42.08	42.25 ± 0.02	3.986	10.75	9.33
Th							
4.00 H_2O	28.57	28.63 ± 0.08	43.32	43.34 ± 0.03	3.995	8.88	9.03
Zr							
5.00 H_2O	13.22	13.27 ± 0.10	51.08	51.36 ± 0.02	4.010	13.06	12.82
Hf							
5.00 H_2O	22.98	23.33 ± 0.02	45.30	45.38 ± 0.05	3.944	11.60	11.66

[a] All ±0.01.

ing. Using the same reasoning as Quagliano, from the shift of the 1400 cm.$^{-1}$ band, the zirconium and hafnium anions would have the same bond character as the aluminum trisoxalato anion, while the uranium and thorium compounds would have somewhat less covalent character.

The zirconium and thorium plus four ions have an inert gas configuration, while hafnium(IV) has the completed 4f shell exposed. Extrapolating Taube's[22] inert-labile concept to coördination number eight, one would expect d^4sp^3 hybridization to leave one d orbital unoccupied, thus accounting for lability of the complexes of these metals. Uranium(IV), on the other hand, has two electrons beyond a completed shell, and its d^4sp^3 complexes conceivably might be expected to possess the filled d-orbitals characteristic of inert complexes. On the basis of magnetic measurements, however, these electrons have been interpreted to be two unpaired f electrons.[23] We have confirmed the paramagnetic nature of $K_4U(C_2O_4)_4 \cdot 5H_2O$ in solution at 25°. It appears, therefore, that if uranium utilizes d^4sp^3 orbitals for bonding there must remain one vacant, low energy d orbital which can contribute to its lability.

Experimental

Preparations.—These preparations, which will be published elsewhere,[24] were based on the observations of other investigators,[10-15] although the final procedures came from no one source. The general method of preparation was to dissolve the normal oxalate in an excess of alkali metal oxalate solution, heat to boiling and, after cooling, precipitate the product by the addition of absolute alcohol. The amount of ethanol had to be carefully regulated to avoid precipitation of potassium oxalate. Analyses are given in Table III.

Analytical Methods.—Since oxalate interfered with the metal determinations it was removed by two successive evaporations with concentrated nitric acid. From an aqueous solution of this paste, the metal oxides were precipitated with aqueous ammonia, and ignited as the oxide. Uranium also was determined by titration of uranium(IV) with permanganate.[25] In some cases combined oxalate and uranium were determined, and the oxalate then was arrived at by difference. The uranium determined as U_3O_8 and by titration were identical. The water content of the uranium compound was always low.

Hydrolysis Experiments.—Appropriate weights of samples were dissolved in water to give 0.01 *M* solutions, and the change in *p*H recorded. After the equilibrium *p*H was reached, ethanol was added to the solution to precipitate the salt which then was dried and analyzed.

Magnetic Susceptibility.—The magnetic moment of the tetraoxalatouranate(IV) was determined in solution; the method used was that described by Schuler.[26] Magnetic moments determined for three uranium solutions of 12.4%, 4.90%, and 2.40% solute were 2.5, 2.1, and 2.6, respectively.

X-Ray Data.—X-Ray powder photographs were taken with a 114-mm. camera using nickel-filtered copper radiation. The sample was contained in a thin quartz capillary and was diluted with gum tragacanth to reduce absorption doubling of the lines. The relative intensities were determined visually. The complete powder patterns will be filed elsewhere,[27] although the strongest lines are given in Table IV. The powder patterns were not indexed completely. The large unit cells and the strong reflecting power of the heavy metal atoms resulted in a large number of lines. The absorption error was quite serious with the copper radiation used and the uncorrected "*d*" values suffer some inaccuracy therefore.

TABLE IV

STRONGEST LINES OF $K_4M(C_2O_4)_4 \cdot nH_2O$

Zr·5H_2O		Hf·5H_2O		U·5H_2O		Th·4H_2O	
d	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0
8.05	100	8.08	100	8.84	100	9.00	100
...	...	...	...	7.47	25	7.56	30
6.61	10	6.62	30	...	...	...	...
5.79	15	5.80	35	5.86	15	5.93	40
...	...	...	...	5.51	20	5.59	50
4.27	5	4.28	15	4.43	15	4.52	50
3.99	10	3.99	30	...	...	...	...
3.77	8	3.82	25	...	...	...	...

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(22) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

(23) T. Ammov, V. Zelenstov, and I. Savich, *Proc. Acad. Sci. U.S.S.R.*, **128**, 533 (1960); Eng. Trans., **128**, 763.

(24) Submitted to "Inorganic Syntheses," Vol. VIII.

(25) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman "Applied Inorganic Analysis," John Wiley and Sons, New York, N. Y., 1953, p. 307.

(26) R. H. Schuler, *J. Chem. Educ.*, **27**, 591 (1950).

(27) Submitted to A.S.T.M. X-Ray Powder Data File, Penna. State Univ., University Park, Penna.

Good single crystals of the thorium and uranium complexes were not obtained. However, suitable specimens were produced for the zirconium and hafnium compounds, and Weisenberg and precession photographs were taken on these. The unit cell dimensions (Å.) are: hafnium compound, $a = 10.64$, $b = 12.35$, $c = 15.94$, and $\beta = 94° 20'$; for the zirconium compound, $a = 10.23$, $b = 12.34$, $c = 16.10$ and $\beta = 94°$. There are four formula units per unit cell.

Densities.—The densities were determined pycnometrically in benzene at 25.0 ± 0.1°. All weights were corrected for air buoyancy. The accuracy is estimated to be ±1%. The values are: U, 2.57 g./cc.; Th, 2.48 g./cc.; Zr, 2.17 g./cc.; and for the Hf compound, 2.44 g./cc. The calculated densities for the zirconium and hafnium compounds are 2.26 and 2.47 g./cc., respectively.

Resolution Experiments.—Measurements of optical activity were made with a Rudolph precision polarimeter whose vernier permitted interpolation to 0.001°. Sodium D light was used. Groups of five measurements were taken and averaged. Average deviations of individual measurements were usually about ±0.005 for such sets. Hence rotations corrected for zero determinations were subject to a maximum error of ±0.01° due to balancing and reading alone. A 1-dm. tube was used. The work of Marchi and McReynolds[9] was repeated. A 0.002 mole sample of potassium tetraoxalatouranate(IV) dissolved in 20 ml. water was added to a solution of 0.004 mole of anhydrous strychnine sulfate in 150 ml. of oxygen-free water. When cooled in an ice bath, the complex strychnine salt began to precipitate. After 10 min. the solution was filtered. The precipitate corresponded to Marchi's "unstable *dextro* isomer," the potassium tetraoxalatouranate recovered from the filtrate corresponded to the "stable *dextro* isomer." Another run was made using different relative concentrations of 0.004 mole strychnine sulfate in 150 ml. of water and 0.00033 mole of the potassium tetraoxalatouranate(IV) in 20 ml. of water. The precipitate obtained here corresponded to Marchi's "stable *levo*" isomer. The fourth or "unstable *levo*" isomer was obtained from the precipitate resulting when a solution of 0.00067 mole strychnine sulfate in 25 ml. of water was added to 0.002 mole of the uranium complex in 10 ml. of water. When this was done no precipitate occurred until after 20 min. After 40 min. the precipitate was filtered. The precipitate and filtrate were freed of strychnine by treating with potassium iodide. The resulting strychnine iodide was removed and the potassium tetraoxalatouranate(IV) recovered from solution by the addition of 500 ml. of ethanol. The rotations measured on the solutions of these samples are given in Table I. In some instances, the uranium complex was not recovered from the iodide solution since it was thought that rapidly racemized isomers would be detected more easily by reason of lesser time of contact with the solution in this method. Experiments also were conducted in which the fractionated salt was dissolved in water and its rotation observed over varying periods of time. In neither case were significant rotations observed.

The attempts to resolve the tetraoxalatozirconate ion were made as follows. Potassium tetraoxalatozirconate 5-hydrate (0.002 mole) dissolved in 25 ml. of water was added to a solution of 6.7×10^{-4} mole of strychnine sulfate in 10 ml. of water. A transient white precipitate appeared, but the solution cleared and 5 min. passed before small clear crystals became visible. After 35 min. the solution was filtered. This process was repeated three more times to give four precipitates in all. After removing the strychnine as the iodide, the filtrates gave rotations of No. 1, 0.002°; No. 2, −0.009°; No. 3, −0.002°; No. 4, −0.003°. In a fractional crystallization experiment on the strychnine tetraoxalatozirconate in which about one-third of the solute was crystallized each time, the second precipitate when freed of strychnine showed a rotation of −0.023°.

Quinine also was studied as a resolving agent for the tetraoxalatozirconate anion. A solution of 0.0142 mole of quinine 3-hydrate in 135 ml. of 0.1 *N* hydrochloric acid was added to a solution of 0.0033 mole of potassium tetraoxalatozirconate in 10 ml. of water. Enough hot water was added to the resulting precipitate to effect complete solution (about 2 l.). The hot solution then was permitted to cool. At 41° the solution was filtered and at 28° a second precipitate was filtered from the solution. Rotations of 0.100-g. samples in 10 ml. of saturated potassium iodide solution were determined after filtration of the quinine iodide. The solution from the first precipitate had a rotation of −0.050° (average of five) and the solution from the second precipitate had a rotation of −0.047°.

A fractional precipitation experiment with quinine hydrochloride also was carried out. Several 0.0013-mole samples of quinine hydrochloride each were dissolved in 25 ml. of water. These portions were added successively to a 0.004-mole sample of potassium tetraoxalatozirconate 5-hydrate in 300 ml. of water. The addition of the first quinine fraction produced no precipitate in an hour at room temperature. The second portion yielded a white precipitate which was filtered 15 min. after the addition. The third portion was added and the solution again filtered after 15 min. One-tenth-g. samples of these two precipitates were treated with 10 ml. of saturated potassium iodide solution and the solutions filtered. The rotations were No. 1, −0.041°; No. 2, −0.041°; and No. 3, −0.047°.

Oxalate Exchange Experiments.—Oxalate exchange was measured by determining the extent to which C-14 tagged oxalate was incorporated into the tetraoxalatometallate anion which originally contained no C-14 activity. A standard sample representing 100% exchange was prepared by weighing out 0.00100 g. of C-14 containing oxalic acid 2-hydrate[28] together with 2.00000 g. of the complex salt. The radioactive oxalate thus was below 0.1% of the total oxalate. The mixture was finely ground and a set of ten 0.01000-g. samples was weighed out on steel planchets. The remainder of the sample then was dissolved in a measured volume of water at a known temperature. The solution was always complete in 15–30 sec. After the desired length of time absolute ethanol was added to precipitate a sample of the tetraoxalate salt and about 1 min. was allowed for crystallization. The precipitate was filtered, washed with 10 ml. of ethanol, and dried by suction. The exchange was considered to have stopped when the precipitate was dry. The shortest time in which this separation could be carried out was about 2 min.

The weighed samples of the standard or reprecipitated salt were slurried with ethanol, dried at 50°, cooled, and weighed. A drop of collodion was added to fix the sample,

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[28] Volk Radiochemical Company—2.6 millicuries C-14 per mmole oxalic acid.

TABLE V

	Al	Zr	Hf	Th	U
H_2O cryst.	3440w	3450m	3425m	3450s	3425m
ν_a(O–C–O),B_1	1725vs				
	1695vs	1660vs	1660vs	1640vs	1620vs
(O–C–O),A_1	1400vs	1400s	1400s	1420s	1420s
ν_s(O–C–O),B_1	1290s	1280m	1280m	1280m	1275m
	1268s				
ν(C–C),A_1	906m	900w	900w	895w	895w
δ(O–C–O),B_1	820m				
	800m	795m	785m	785m	783m
	577s	582m	588s	. . .	582w
	. . .	524s	529s	. . .	. . .
	478s	492s	492s	490s	495s
		. . .	. . .	. . .	460s
	434m	. . .	. . .	. . .	. . .
	. . .	. . .	. . .	. . .	398w
	. . .	377w	375w	381m	387w
	. . .	. . .	. . .	. . .	376w
	365w	365w	365w	363w	364w

the sample redried at 50°, and reweighed. The weight taken was between infinite thinness and infinite thickness. The infinite thickness method was not used because of the necessity for keeping the uranium counting rate low with respect to the C-14. The uranium standard samples measured without C-14 beta radiation were counted with a thin-wall window Geiger tube.

In several series of trial weighings on ten standard samples, the average deviation of a single measurement was less than 0.00002 g. and the deviation of the mean of of five measurements was less than 0.00001 g. The error in weights of C-14 oxalic acid of the order of 0.00100 g. was thus about 2%.

The average deviation of counting rates of individual samples in sets of ten varied between 2 and 5%. At the level of total counts recorded (10,000 per sample), the average deviation due to chance alone was 1%. Thus the deviation due to sample mounting technique alone was not excessive. The average deviation of the mean of sets of ten samples was 0.5 to 1.7%. Therefore variations of up to about 4% were expected in duplicate exchange runs. For samples made up as described, the calculation is

$$\%\ \text{exchange} = 100 \times \frac{c/m \text{ due to C-14 in exchanged sample}}{c/m \text{ due to C-14 in standard sample}}$$

In some cases additional non-active potassium oxalate-1-hydrate was added to the sample. In this instance the calculation becomes

$$\%\ \text{exchange} = 100 \times \frac{c/m \text{ due to C-14 in exchanged sample}}{c/m \text{ standard sample} \times \dfrac{\text{oxalate in complex}}{\text{oxalate-total}}}$$

The results of the exchange experiments are given in Table II.

Spectra.—The infrared spectra of the potassium oxalatometallates were run over the range 4000–625 cm.$^{-1}$ using the potassium bromide pellet technique and the Baird infrared spectrophotometer with a sodium chloride prism. Over the range 650 to 350 cm.$^{-1}$ the Nujol mull technique and the Perkin–Elmer Model 112 infrared spectrophotometer were used. The major bands are given in Table V. The assignments are those Quagliano[21] made for the tris-oxalatometallates.

Acknowledgment.—The authors wish to thank Professors L. Dahl and M. Evans of this department for consultations on the X-ray and infrared work.