Table IV (*Concluded*)

Class	Configuration	Optically active	Optically inactive	Total
3AA 2b	C	2	2	4
	A	16	1	17
	P	2	3	5
	D	34	2	36
3AB 2c	C	20	0	20
	A	94	0	94
	P	20	6	26
	D	242	6	248
4AA	C	0	2	2
	A	6	0	6
	P	0	1	1
	D	10	1	11
4AB	C	6	5	11
	A	42	0	42
	P	6	4	10
	D	110	5	115

The authors are indebted to Mrs. Barbara J. Miller, neé Everhart, for assistance in the construction of models and to Professors E. N. Lassettre and J. K. Senior for their interest and assistance in the mathematical portion of the work.

Summary

Complete isomer tables for monodentate and partial isomer tables for bidentate groups for four likely configurations for compounds of elements exhibiting coördination number eight—the cube, the square Archimedean antiprism, a dodecahedron with triangular faces and symmetry V_d and a trigonal prism with two extra bonds along the unique axis—have been developed.

Columbus, Ohio Received October 21, 1942

[Contribution from the Chemical Laboratory of The Ohio State University]

The Stereochemistry of Coördination Number Eight. Optical Activity of Potassium Tetra-oxalato-uranium-IV[1]

By Louis E. Marchi[2] and James P. McReynolds

The study of the structural configuration of compounds of elements exhibiting coördination number eight has been carried out chiefly by the use of X-ray crystal analysis.[3,4,5]

The authors[6] have carried out a study of the isomer requirements of four types of configuration which are possible for coördination number eight. The configurations considered are the cube (C), the square Archimedean antiprism (A), a trigonal prism (P) with two extra bonds along the unique axis, and a dodecahedron (D) with triangular faces and symmetry V_d. The isomer count for compounds containing four symmetrical bidentate groups 4AA, such as the oxalate group, is given for each of the four structures in Table I.[6] The number of isomers for this type of compound is so large that a complete proof of structure by isomer isolation does not seem possible. However, the proof of the presence of optical isomers will rule out two structures, the cube and the trigonal prism. This study was carried out to determine if such an elimination could be made by chemical methods and shows that the elimination can be made.

Table I

Isomers for Compounds Having Four Symmetrical Bidentate Groups

Class symbol	Configuration	Optically[a] active	Optically inactive	Total
4AA	C	0	2	2
	P	0	1	1
	A	6	0	6
	D	10	1	11

[a] Optically active isomers are listed as individuals, the number of racemic pairs represented is one-half the number listed.

Experimental

Resolution of Potassium Tetra-oxalato-uranium-IV

1. Potassium tetra-oxalato-uranium-IV was prepared by the method of Kohlschütter.[7] However, the starting material was $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ instead of uranyl ammonium carbonate. The product was purified by repeating the precipitation from water solution by alcohol.

2. Resolution was attempted with brucine, cinchonine and strychnine. The brucine salt was too insoluble and the cinchonine salt was too soluble to give good fractionation. The strychnine salt was not sufficiently soluble to carry out satisfactory fractional crystallization but its

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(1) This article is abstracted from a dissertation presented by Louis E. Marchi to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy (August, 1942).

(2) Present Address: Department of Chemistry, Indiana University, Bloomington, Ind.

(3) Natta, *Gazz. chim. ital.*, **58**, 870 (1928).

(4) Hoard and Nordsieck, This Journal, **61**, 2853 (1939).

(5) Hoard, paper presented before the Sixth Annual Symposium, Division of Physical and Inorganic Chemistry, American Chemical Society, Columbus, Ohio, Dec. 29–31, 1941.

(6) Marchi, Fernelius and McReynolds, This Journal, **65**, 329 (1943).

(7) Kohlschütter and Rossi, *Ber.*, **34**, 1472 (1901); Kohlschütter, *ibid.*, 3619.

character was such that fractional precipitation could be carried out. The potassium tetra-oxalato-uranium-IV was recovered from the strychnine salt by Werner's method,[8] *i. e.*, the precipitation of insoluble strychnine iodide with potassium iodide. After the polarimetric examinations were completed the absence of strychnine was shown by the well-known color tests,[9] using for comparison a known strychnine sulfate sample and a known potassium tetra-oxalato-uranium-IV sample. Due to the ease of oxidation of the alkaloid salts of the uranium complex ion, repeated fractionation to obtain high purity for the optical forms was not practical. The fractional precipitations were repeated a number of times in order to observe and check the stability of the four different isomers indicated.

The procedure for a typical run is given below. A 3.46-g. sample of strychnine sulfate pentahydrate was dissolved in 150 ml. of hot freshly boiled water; since the solution was slightly cloudy, "Super-cel" was added, the solution filtered and then cooled as oxygen-free nitrogen passed through it. One and sixty-seven hundredths grams of uranium salt was dissolved in 20 ml. of the warm freshly boiled water and was added to the strychnine sulfate solution. After five minutes, no precipitate had formed, so the solution was cooled in ice. Shortly afterward the strychnine salt began to precipitate out; at the end of five minutes, it was filtered, the entire filtrate placed in a beaker containing 25 g. of finely powdered potassium iodide and the mixture stirred. The potassium iodide went into solution rapidly and the silky strychnine iodide precipitated out. The beaker which contained this material was kept in an ice-water bath during the reaction. The silky precipitate was filtered off and the filtrate passed into 500 ml. of absolute alcohol which was placed in the suction flask to precipitate the potassium salt of the uranium complex. The potassium salt was filtered off, washed with four 25-ml. portions of absolute alcohol and finally ether. A 0.47% solution when examined in the polarimeter gave a reading of +0.07 ± 0.02° (temperature, 31°). After twelve hours the reading was unchanged.

Evidence for the existence of a stable *levo* form was obtained when the potassium salt was prepared as described above from the filtrate (volume 210 ml.) resulting from the mixture of 3.46 g. of strychnine sulfate and 0.28 g. of potassium tetra-oxalato-uranium-IV. A 0.05% solution gave a polarimeter reading of −0.05 ± 0.02°, which did not change over a twelve-hour period.

A 0.26% solution of the potassium salt obtained from the least soluble fraction (the precipitate from the reaction between 3.46 g. of strychnine sulfate and 1.67 g. of the uranium complex) gave a reading of +0.10°, which fell to 0° over a period of twenty-nine minutes.

The final fraction was obtained by adding a solution of 1.67 g. of the potassium uranium oxalate in 10 ml. of water to a solution of 0.58 g. of strychnine sulfate in 25 ml. of water. After twelve minutes no precipitate had formed. Some precipitate was discernible after twenty-five minutes and the precipitation was assumed to be complete after forty minutes. The solution was filtered, treated with potassium iodide, filtered to remove strychnine iodide and examined in the polarimeter. The concentration of the solution was not known exactly. The observed reading was −0.10° and fell to 0° in forty-three minutes. Dr. Eugene Talley independently checked the change in rotation of the above solution.

The data relating to these isomers are collected in Table II. All the polarimeter readings reported were made with a Schmidt–Haensch polarimeter scaled to 0.01° using the sodium D line as given by a monochromator. The tube length for all readings was 2 dm.

The strychnine salt of the uranium oxalate ion was shown to be tetrastrychnine tetra-oxalato-uranium-IV by analysis. *Anal.* Calcd. for $(C_{21}H_{22}N_2O_2)_4\cdot H_4[U(C_2O_4)_4]\cdot 12H_2O$: U, 11.08; C, 51.44; H, 5.44; N, 5.22; H_2O, 10.06. Found: U, 11.4; C, 49.21; H, 5.23; N, 5.37; H_2O, 10.2.

TABLE II

ROTATION, CONCENTRATION AND STABILITY OF THE FOUR FRACTIONS ISOLATED

Fraction[a]	Observed rotation°[b]	Concentration, %	Final rotation
1	+0.10	0.26	0.00 (29 min.)
2	−0.10	?	0.00 (43 min.)
3	+0.07	0.47	+0.07 (12 hr.)
4	−0.05	0.05	−0.05 (12 hr.)

[a] Fractions numbered according to solubility: 1 is least soluble. [b] Rotations given are read to ±0.02°.

Discussion

The isolation of optical isomers for the compound potassium tetra-oxalato-uranium-IV is seen from Table I to eliminate from consideration two configurations, the cube and the trigonal prism, and any other conceivable configurations which could not give rise to optical isomers. After this elimination, there remains the square Archimedean antiprism and the dodecahedron which may be considered as possible configurations, as well as any other conceivable configuration which could give rise to optically active isomers for this type of compound. The data obtained do not distinguish between the antiprism and the dodecahedron, since to eliminate the antiprism, it would be necessary to isolate more than six different optical isomers, which has as yet not proved practicable, or to prove the presence of an optically inactive form, a procedure which is practically impossible. The elimination of the dodecahedron by an isomer count seems even more difficult because it would be necessary to prove the absence of optically inactive forms.

It is interesting and perhaps significant to note that both the configurations which are considered here as possibilities, have been reported from X-ray crystal analysis. Hoard and Nordsieck[4] report the dodecahedron structure for the molyb-

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(8) Werner, *Ber.*, **45**, 3061 (1912).

(9) Henry, "The Plant Alkaloids," Blakiston's Sons, Philadelphia, Pa., 1939, p. 507.

denum octacyanide ion and Hoard[5] reports the antiprism structure for the tantalum octafluoride ion.

Kimball[10] has examined three of the four configurations considered here in terms of the bonding orbitals necessary to obtain each structure. On this basis he eliminates the cubic structure since it would involve *f* orbitals, no example of which has been authenticated. The antiprism and the dodecahedron could both involve the same orbitals, d^4sp^3.

At present it seems that the antiprism and the dodecahedron structures satisfactorily account for the structure of coördination number eight but that in all likelihood the nature of the ligands will be important in determining which of the two structures applies to a specific compound.[11]

Summary

1. Optical activity in compounds of elements exhibiting coördination number eight is established for the first time by the resolution of $K_4[U(C_2O_4)_4]\cdot 5H_2O$ into four isomers: one *d* and one *l* easily racemized modification and one *d* and one *l* stable modification by fractional precipitation of the strychnine salt.

2. A partial proof of the structure for compounds of elements exhibiting coördination number eight containing symmetrical bidentate groups is made, inasmuch as any structure not requiring optical isomers for the type of compound studied must be ruled out. The cube and the trigonal prism with two extra bonds along the unique axis are ruled out. The data are not sufficient to distinguish between the square Archimedean antiprism and the dodecahedron with triangular faces and symmetry V_d.

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[10] Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

[11] The trigonal prism discussed by Hoard and Nordsieck[4] and by Kimball[10] which was derived from the trigonal prism by placing the extra two groups along the normal to two of the rectangular faces was not considered in detail by the authors but a cursory examination indicates that it would show optical isomers for compounds of the class 4AA. For this reason it is also a possible form for the uranium complex.

[CONTRIBUTION FROM THE INSTITUTE OF EXPERIMENTAL BIOLOGY, UNIVERSITY OF CALIFORNIA]

Kinetics of Hypoiodite Decomposition[1]

BY CHOH HAO LI AND CAROLYN F. WHITE

When iodine dissolves in a highly alkaline solution, hypoiodite ion is formed

$$I_2 + 2OH^- \rightleftharpoons OI^- + I^- + H_2O \qquad (1)$$

and it decomposes with measurable rate into iodate and iodide

$$3OI^- \rightleftharpoons O_3I^- + 2I^- \qquad (2)$$

The kinetics of this reaction has been studied extensively by Forster[2a] and by Skrabal.[2b] These investigators added arsenite in excess to stop the reaction by reacting with hypoiodite and any iodite present and determined the excess at *p*H near to 7 by the titration with triiodide. The second order specific rate was, in general, relatively low in the early stage of an experiment and approached a constant value.

In a recent study of the kinetics of di-iodotyrosine formation,[3] it was proposed to use the phenol reaction to follow the decomposition of hypoiodite ion. This method is based on the fact that phenols react with hypoiodite ion rapidly but not with the iodate which is later determined by titrating the triiodide in acid solution; it has an advantage over the arsenite method in that it enables an accurate determination of the initial rate to be made, since the small amount of the product then present may be determined directly and not as the difference of two large titration values. Using this method, we have confirmed the conclusions of Forster and Skrabal that the rate of reaction (2) at sufficiently high concentrations of hydroxide and iodide ions is proportional to the concentration of hypoiodite ion, hypoiodous acid and iodide ion. In addition, we have found that the reaction can also proceed through another path which requires only two hypoiodite ions.

The Rate Law.—The rate of reaction (2) in each experiment obeys equation (3)

$$-d(OI^-)/dt = k(OI^-)^2 \qquad (3)$$

and *k* is a function of the concentrations of hydroxide and iodide ions. The increase in the con-

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[1] Aided by grants from the Board of Research of the University of California and the Rockefeller Foundation, New York City.

[2a] E. C. L. Forster, *J. Phys. Chem.*, **7**, 640 (1903).

[2b] Skrabal, *Monatsh.*, **32**, 167, 185 (1911); **33**, 99 (1912). References to other investigations in this field will be found in the papers cited in "I.C.T.," VII, 149 (1930). See also Bray, THIS JOURNAL, **52**, 3580 (1930); Chapin, *ibid.*, **56**, 2211 (1934).

[3] Li, *ibid.*, **64**, 1147 (1942).