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The Crystal Structure of Ceric Iodate Monohydrate*

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Ceric iodate monohydrate crystallizes in space group C_{2h}^5–$P2_1/n$, with four molecules in the unit cell of dimensions $a = 9{\cdot}57$, $b = 14{\cdot}92$, $c = 8{\cdot}00$ Å, and $\beta = 97°\ 35'$. The crystal structure has been determined from a three-dimensional Patterson function and refined by a three-dimensional difference Fourier. The structure is composed of discrete, trigonal iodate groups with average distances I–O = 1·82 Å and O–O = 2·74 Å. Each of two oxygens per iodate group is shared with cerium, but the third is not. The cerium atom has seven oxygen neighbors at 2·18–2·41 Å and one at 2·82 Å, which form a much distorted Archimedes antiprism. Each iodine atom has three oxygen neighbors at 1·77–1·86 Å and three others at 2·5–3·1 Å, which form a much distorted octahedron. Two of the iodine atoms require the oxygen atom from the water molecule to complete this octahedral arrangement.

Introduction

This investigation of the crystal structure of ceric iodate monohydrate, $Ce(IO_3)_4.H_2O$, was undertaken both to resolve the serious disagreement (Wells, 1949) in previous determinations of the dimensions of the iodate group, and because of the current interest in structures of compounds of rare earths, which are often isomorphous with analogous compounds of the transuranics. It incidentally tested the detail and accuracy obtainable from a three-dimensional Patterson function based upon extensive intensity data from an inorganic compound.

Preparation, chemical analyses, and properties

Well-crystallized samples of what was thought to be anhydrous ceric iodate, prepared by the slow homogeneous oxidation of cerous nitrate in 8N nitric acid by excess iodic acid, were kindly supplied by Prof. H. H. Willard of the University of Michigan. The soft, deep-yellow crystals are insoluble in water, but soluble in concentrated nitric acid.

Earlier preparations of ceric iodate by Prof. Willard were found by other investigators (Staritzky & Walker, 1952) to be tetragonal‡. The material reported upon here, however, is shown by Laue photographs and by its habit to be monoclinic. The crystals are occasionally almost cubes, but appear generally as truncated pyramids; this latter hemimorphic habit, in view of evidence for a center of symmetry (see below), is presumably only an accident of growth. It was thought during most of this investigation that anhydrous ceric iodate was dimorphic, and that the monoclinic form was being studied. The first evidence that the material under investigation was the monohydrate and not the anhydrous compound was obtained from the difference Fourier (see below). Accordingly, chemical analyses were performed; these analyses confirmed that the substance was indeed ceric iodate monohydrate.

Cerium was determined by igniting the sample to CeO_2 at 700–800° C. The ignition was actually carried out in air at the rate of $2\frac{1}{2}$° C./hr. on a Chevenard thermobalance; the weight-loss versus temperature curve shows some interesting features which will be discussed in a later section. Iodate was determined in the following way: The sample was dissolved in potassium iodide solution, and the resultant iodine was titrated with thiosulfate. Iodate was then determined from the titer, after correction for the amount of tetrapositive cerium known to be present. Such analyses gave: Ce, 16·5%; IO_3, 81·2%; remainder, 2·3%. The values predicted for $Ce(IO_3)_4.H_2O$ are Ce, 16·3%; IO_3, 81·6%; H_2O, 2·1%, and those for $Ce(IO_3)_4$ are Ce, 16·8%; IO_3, 83·2%.*

A test for the piezoelectric effect was negative.†

The density measured pycnometrically on two powdered samples with water as the liquid was 4·89±0·03 g.cm.$^{-3}$ at 27° C.

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‡ The study of tetragonal ceric iodate, which was discontinued after a determination of the cell dimensions and symmetry, has been resumed (Cromer, 1954).

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† I am indebted to Dr W. G. Sly of these Laboratories for making this test on a modified Giebe & Scheibe apparatus which had an oscillation range of 0·4–7·5 megacycles/sec.

Unit cell and space group

Equatorial measurements on rotation photographs prepared with nickel-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) and indexed with the guidance of Weissenberg photographs gave

$$a = 9{\cdot}57\pm0{\cdot}01,\ b = 14{\cdot}92\pm0{\cdot}02,\ c = 8{\cdot}00\pm0{\cdot}02\ \text{Å},\ \beta = 97^\circ\ 35'\pm15'\ .$$

The density calculated for four molecules in the unit cell is then $5{\cdot}03\pm0{\cdot}03$ g.cm.$^{-3}$.

On Weissenberg photographs prepared as described below the only systematic extinctions were for $0k0$ with k odd and $h0l$ with $h+l$ odd. The space group is therefore C_{2h}^5–$P2_1/n$.

Collection of intensity data

Ceric iodate monohydrate absorbs X-rays so strongly, the linear absorption coefficient μ being 1285 cm.$^{-1}$ for Cu $K\alpha$ and 161 cm.$^{-1}$ for Mo $K\alpha$, that a convenient and sufficiently reliable correction for absorption seemed impossible except for a spherical specimen with relatively hard radiation. (Sample values of A, the ratio of intensity with absorption to intensity without absorption, for a cubic specimen 0·0059 cm. on an edge with Mo $K\alpha$ are 0·38 for Bragg angle 0° with incidence normal to a face, and 0·48 for Bragg angle 90° with incidence along a face diagonal. Corresponding values for Cu $K\alpha$ are 0·0005 and 0·088.) A grinder patterned after the design of Bond (1951) readily reduced the crystals to nearly perfect spheres, and one of these with maximum diameter 0·0097 cm. and minimum diameter 0·0091 cm. was selected for the Weissenberg photography.

Equi-inclination photographs were taken with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) in a Weissenberg camera of radius $90/\pi$ mm. A strip of zirconium metal 0·038 mm. thick was interposed between the layer-line screen and the film, to filter the molybdenum radiation and to remove the fluorescent cerium L and iodine L radiations. The multiple-film technique was used with five photographic films interleaved with copper sheets 0·025 mm. thick. The experimental film factors, corrected for the obliquity factor, ranged from 3·1 to 3·5. Exposures of about 2,000 mA.hr. gave data out to $\sin\theta/\lambda = 1{\cdot}0$. The entire volume of the reciprocal lattice which lies within this range contains about 9,600 non-equivalent points; it was covered by photographs around the a and c axes up to an equi-inclination angle μ of 30°. Data were thus collected from the reciprocal-lattice nets $h = 0, 1, \ldots, 13$ and $l = 0, 1, \ldots, 11$. The few low-order reflections which were hidden by the beam stop on the photographs prepared with Mo $K\alpha$ were observed on zero- and first-layer photographs around a and c prepared with filtered Cu $K\alpha$ radiation. About 35% of the reflections within the sphere $\sin\theta/\lambda \leq 1{\cdot}0$ were unobservably weak.

The intensities were estimated visually with the aid of an intensity strip. The strip had a scale of intensity from 1 to 100 with the weakest spot barely visible; it was prepared from multiple oscillations at constant speed through the 080 reflection. The crystal gave round reflections of uniform size on an even, light background.

Reduction of intensities to $|F|$ values

Only full application of machine methods for bookkeeping and calculations made possible the reduction of the numerous intensity data to $|F|$ values. I.B.M. punched cards and machines were used throughout.

The observed intensities were corrected for absorption with the aid of Evans & Ekstein's table (1952), and were multiplied by the Lorentz and polarization factors

$$\frac{4\cos\theta}{1+\cos^2 2\theta}\,(\sin^2\theta-\sin^2\mu)^{\frac{1}{2}}\ .$$

No correction was applied for extinction; the effect of extinction, however, was probably minimized by the grinding. The intensities from all layer lines were adjusted to a common scale by a cyclic procedure.

Reduced intensities estimated from both the a- and c-axis photographs were averaged: $I = \frac{1}{2}(I_a+I_c)$. They were also differenced to obtain $r = |I_a-I_c|/I$, which provides a measure of reliability; r was computed for each of 4,255 non-equivalent reflections which were observed to be non-zero around both axes. As a function of I, $\bar{r}$ shows the expected trend: At very low I ($I \leq 5$, 1,061 reflections) $\bar{r}$ is 0·17; at low I ($5 < I \leq 10$, 1,161 reflections) $\bar{r}$ is 0·11; at intermediate and high I ($10 < I \leq 199$, 2,014 reflections) $\bar{r}$ is 0·07; at very high I ($199 < I \leq 500$, 19 reflections) $\bar{r}$ is 0·12. The overall average of $\bar{r}$ is 0·108.

A scale factor of 492 and a B value (in the temperature factor $\exp(-B\sin^2\theta/\lambda^2)$ for amplitude) of 0·81 Å^2 were derived by Wilson's method (1942) on the assumption of form factors calculated from the Thomas–Fermi potential and corrected for K-electron dispersion (James, 1950) for cerium and iodine, and of the McWeeny $\bar{f}$ (1951) for oxygen.

The determination of the structure

(a) *The three-dimensional Patterson function*

The three-dimensional Patterson function, with the peak at the origin removed, was calculated at intervals of $\frac{1}{60}$th of the cell edges with the M-card system devised by Prof. Verner Schomaker. The actual calculation required about 60 man-hours and about 75,000 I.B.M. cards.

The five heavy atoms were located without difficulty. Their interactions, which should give rise to 55 peaks in the asymmetric quarter cell, 50 of height 20,000 e.^{2}Å^{-3}, 5 of height 10,000 e.^{2}Å^{-3}, and all of half-width 0·28 Å at half height, account for all the Patterson peaks of height 10,000 e.^{2}Å^{-3} or greater; 39 of these peaks are very well resolved. The heavy-atom coordinates (Table 1) were refined by a cyclic procedure similar to the one described by Shoemaker, Barieau, Donohue & Lu (1953), but here restricted to the well-resolved peaks. The cerium atom was recognized both from the peak heights and from the distances and numbers of nearest neighbors.

Table 1. *Coordinates of the atoms in the asymmetric unit cell*

	Determined from the Patterson function			Refined from the difference Fourier		
Ce	0·624	0·239	0·029	0·6233	0·2385	0·0285
I						
1	0·365	0·116	0·263	0·3663	0·1158	0·2641
2	0·837	0·425	0·263	0·8362	0·4249	0·2634
3	0·934	0·087	0·217	0·9340	0·0868	0·2169
4	0·288	0·378	0·150	0·2882	0·3778	0·1498
O						
1	—	—	—	0·394	0·000	0·328
2	0·53	0·15	0·20	0·550	0·140	0·239
3	0·34	0·16	0·45	0·370	0·169	0·472
4	—	—	—	0·781	0·484	0·443
5	0·97	0·36	0·40	0·957	0·349	0·387
6	0·68	0·35	0·22	0·686	0·348	0·229
7	—	—	—	0·850	0·032	0·383
8	0·08	0·15	0·33	0·075	0·141	0·356
9	0·81	0·17	0·17	0·814	0·185	0·184
10	0·40	0·47	0·27	0·401	0·455	0·268
11	0·21	0·33	0·34	0·223	0·320	0·324
12	0·44	0·30	0·10	0·412	0·290	0·111
w	—	—	—	0·08	0·23	0·02$_5$

Since the interactions of heavy atoms with oxygen atoms should lead to 260 peaks of height 1,700 e.^{2}Å^{-3} and half-width 0·4 Å, finding the oxygen atoms from the Patterson, with its general background of from -500 to $+1{,}000$ e.^{2}Å^{-3}, is much more difficult than finding the heavy atoms. Nevertheless, this was done. The identifications of the heavy-atom–heavy-atom peaks having been established, a modified superposition method was used. All vectors connecting peaks of height greater than 3,000 e.^{2}Å^{-3} but less than 10,000 e.^{2}Å^{-3} were listed and compared with the heavy-atom–heavy-atom peak positions. The coincidences constituted tentative determinations of oxygen positions* which had to be confirmed or rejected by repeated consistent occurrence and structural reasonableness. Nine oxygen positions (Table 1) were found in this way. The remaining three, O_1, O_4 and O_7, which were not so determined, were inferred from the position of O_{10}. (At this point in the investigation the compound was thought to be anhydrous, and so the presence of O_w was not suspected.)

By these steps an approximate structure for ceric iodate was derived from the Patterson function. To refine the structure a difference Fourier was next computed.

(b) Calculation of partial structure factors

From the coordinates of the five heavy atoms their contributions F'_c to the structure factors were calculated for the 2,700 reflections which lie within the sphere $\sin\theta_{\text{Mo}} \leq 0{\cdot}46$, that is, within the limiting sphere for copper radiation. After a least-squares refinement of the scale and temperature factors, the R factor $\Sigma|F_o-F'_c|\div\Sigma|F_o|$ was 0·16 with F_o for unobserved reflections taken as 0, and 0·14 with unobserved reflections omitted. Only very small changes were found in the scale and temperature factors; the final value of B is 0·82 Å^2.†

(c) The three-dimensional difference Fourier

A difference Fourier with coefficients $F_o-F'_c$ was computed in intervals of $\frac{1}{60}$th of the cell edges with the *M*-card system.

The general background level of the difference Fourier is between -3 and $+3$ e.Å^{-3}. There are twelve sharp peaks of height approximately 14 e.Å^{-3} and half-width 0·3 Å, one diffuse peak of height 8 e.Å^{-3} and half-width 0·6 Å, and some variations as large as 10 e.Å^{-3} near the heavy-atom positions.

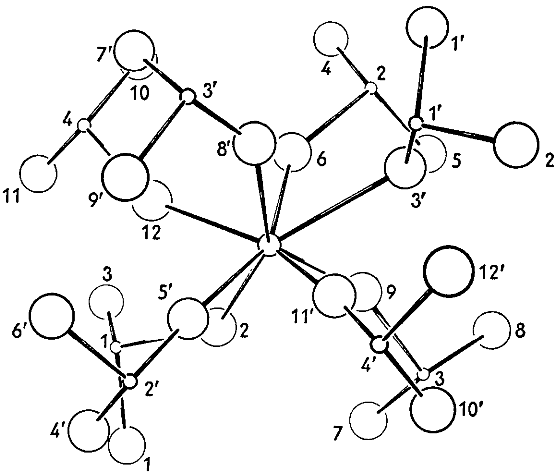

Fig. 1. The arrangement of iodate groups around a cerium atom. This is a normal projection on to the *ab* plane. In order of increasing size, the circles represent iodine, cerium and oxygen.

The twelve sharp peaks are due to oxygen atoms; they are nearly spherical with average height corresponding to a B of 2·7 Å^2. The peak centers were located by fitting Gaussians to central groups of twenty-seven points by least squares (Shoemaker,

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* That is, if $\mathbf{r}_{MO}-\mathbf{r}_{NO'} = \mathbf{r}_{M'N'}$, the primed and unprimed atoms *may* be respectively identical so that $\mathbf{r}_O = \mathbf{r}_{MO}+\mathbf{r}_M = \mathbf{r}_{NO'}+\mathbf{r}_N$. Thus, $\mathbf{r}_O$ is then determined, since $\mathbf{r}_M$ and $\mathbf{r}_N$ are already known.

† The 2,700 F'_c values and the 9,600 $|F|$ values can be made available to anyone interested in further refinement of the structure. These data might also prove of value in testing new statistical techniques or methods.

Table 2. *Interatomic distances*

(Values in Ångström units)

Cerium–oxygen
(< 4·0 Å)

Ce–O		Ce–O	
11′	2·18	12	2·34
9	2·22	2	2·41
5′	2·25	3′	2·82
8′	2·28	4‴	3·91
6	2·31	9′	3·94

Cerium–iodine
(< 4·5 Å)

Ce–I		Ce–I	
1	3·77	1′	3·99
2	3·80	4′	3·99
3	3·88	4	4·05
3′	3·89	2′	4·06

Iodine–iodine
(< 4·2 Å)

I–I		I–I	
2–3‴	3·56	1–4	4·06
3–4′	3·94	1–2′	4·09
1–4‴	3·94	1–3	4·13
1–2′	4·02	3–4‴	4·15
1–2‴	4·05		

Iodine–oxygen
(< 3·2 Å)

I_1–O		I_2–O	
1	1·81*	4	1·82*
2	1·83	5	1·82
3	1·84	6	1·83
12	2·93	7‴	2·56
4′	2·99	3′	2·78
8	3·00	1‴	2·99

I_3–O		I_4–O	
8	1·82	10	1·77*
7	1·83*	11	1·82
9	1·86	12	1·82
10‴	2·51	1‴	2·55
4‴	2·73	7′	2·66
w	3·1	*w*	3·0

* Not shared with cerium.

Oxygen–oxygen
(intra-iodate)

O–O		O–O	
1–2	2·72	7–8	2·73
2–3	2·73	8–9	2·77
1–3	2·79	7–9	2·78
4–5	2·70	11–12	2·68
4–6	2·73	10–11	2·71
5–6	2·73	10–12	2·77

Oxygen–oxygen
(inter-iodate ≤ 3·1 Å)

O–O		O–O		O–O		O–O	
3–*w*′	2·5	3–11	2·83	9–11′	2·90	2–*w*′	3·0
5–11	2·69	4–7‴	2·83	11–*w*	2·9	7–10‴	3·03
2–9	2·71	2–5′	2·84	11–*w*′	2·9	6–8′	3·04
2–12	2·73	3–9′	2·86	1–10‴	2·91	8–11	3·05
6–9	2·77	3–8	2·88	8–12′	2·91	7–10′	3·06
6–12	2·80	3–6′	2·89	8–10‴	2·97	9–*w*	3·1
5–12′	2·81	6–7‴	2·89	8–*w*	3·0		

The equivalent positions are x, y, z; $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$ (′); $\bar{x}, \bar{y}, \bar{z}$ (″); $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$ (‴).

Donohue, Schomaker & Corey, 1950), which on a desk calculator takes only about 15 min. per peak. All twelve original oxygen positions were confirmed; the average shift for the nine that had been derived directly from the Patterson was 0·25 Å.

Shifts of the heavy atoms averaging 0·005 Å were obtained from the corresponding features of the difference Fourier, but no significant changes in the original isotropic temperature factor are indicated. The shifts were evaluated on the assumption of Gaussian peak shapes

$$\varrho(r) = \varrho(0) \exp\left\{-\pi(\varrho(0)/f(0))^{\frac{2}{3}}r^2\right\},$$

with $\varrho(0)$ set equal to the integral of the product of form and temperature factors over the spherical volume in reciprocal space bounded by the limiting value of $\sin\theta/\lambda$ (Hamilton, 1954). The values used here ($B=0·82$ Å^2, $\sin\theta_{\text{Mo}}(\text{max.})=0·46$, $f_{\text{Ce}}(0)=56·7$, and $f_{\text{I}}(0) = 51·7$) give $\varrho(0)$ values of 235 for cerium and 210 for iodine.

The single diffuse peak is assigned to the oxygen atom O_w from the water molecule. The height of the peak corresponds to a value of B of about 6 Å^2. No indication of the positions of the hydrogen atoms could be obtained from the difference Fourier.

The coordinate values are collected in Table 1.

Description of the structure

Ceric iodate monohydrate contains discrete iodate groups which are trigonal within the precision of this study. Each of two oxygen atoms per iodate group is shared with a different cerium atom, but the third is not. Each cerium atom has seven nearest oxygen atoms at 2·18–2·41 Å, another oxygen atom at 2·82 Å, and two much further away at 3·91 and 3·94 Å. The eight nearest oxygen atoms form a much distorted Archimedes antiprism, or alternatively a trigonal prism with two oxygens above the centers of two of the three sides. (The oxygen atom at 3·91 Å faces the remaining side.) Cerium atoms share none of the eight oxygen atoms with each other.

Each iodine atom, in addition to its three oxygen neighbors at 1·77–1·86 Å, has three more at 2·5–3·1 Å. The six oxygen atoms are arranged at the corners of a much distorted octahedron. A similar octahedron is found in α-iodic acid (Rogers & Helmholz, 1941). It should be noted that if the diffuse, extra peak in the difference Fourier were assumed to be spurious, for example to result from incorrect form factors for the heavy atoms, rather than to be assigned to an oxygen atom from a water molecule, two of the four iodine atoms would have only five oxygen neighbors. Moreover, a tunnel of diameter about 3 Å would run through the structure approximately parallel to the *b* axis (Fig. 2). There was thus a strong indication that the peak was real and due to an oxygen atom from a previously unsuspected water of hydration. Chemical analyses were performed, and they confirmed this indication.

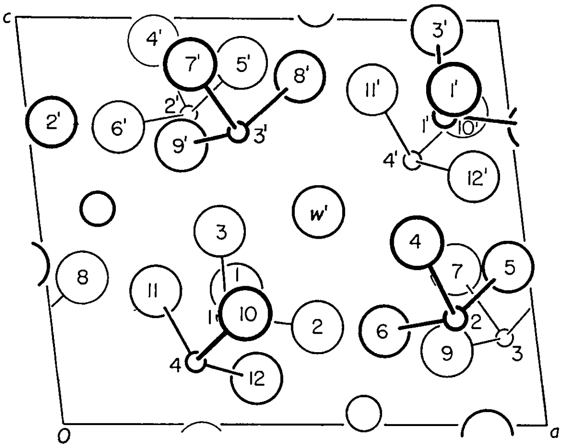

Fig. 2. A normal projection on to (010) of one-half the unit cell; the half not included is generated by a center at ½, ½, ½.

Each oxygen atom has from three to eight oxygen neighbors at a distance less than 3·10 Å.

Table 2 lists some of the interatomic distances which may be computed from the coordinates of Table 1 and from the unit-cell dimensions. Cruickshank's method (1949, 1954),

$$\text{i.e.}\quad \sigma(x_n) = \overline{(\partial(\varrho_o-\varrho_c')/\partial x)^2}^{\frac{1}{2}}/(\partial^2\varrho_{cn}/\partial x^2)\ ,$$

was applied to the difference Fourier in order to estimate the standard deviations of these interatomic distances. The method gave σ(O) = 0·014 Å, σ(I) = σ(Ce) = 0·001 Å. An approximate calculation indicated that these values are not much higher than those which would be obtained from a difference Fourier computed from structure factors which included the oxygen contributions. Thus, σ(*M*–O) = 0·014 Å, σ(O–O) = 0·020 Å, and σ(*M*–*M*) = 0·0014 Å. Because of the diffuseness of the peak assigned to O_w, standard deviations of those distances which involve O_w are higher, probably around 0·1 Å.

The distances I–O = 1·823±0·021 Å and O–O = 2·737±0·034 Å are obtained on the assumption that all the iodate groups are equivalent and trigonal. In view of the fair agreement of these standard deviations with those obtained by Cruickshank's method, significant variations in the I–O or O–O distances in ceric iodate monohydrate seem rather unlikely. (The mean I–O and O–O distances on the assumption of equivalent, trigonal iodate groups are thus 1·823 ±0·006 Å and 2·737±0·010 Å. The mean O–I–O angle is then 97° 8′±20′.)

Comparison with other structures

The packing density in this compound is typical for iodate structures. The volume per oxygen atom is 21·8 Å^3 in ceric iodate monohydrate compared with 24·7 in sodium iodate, 20·8 in α-iodic acid, about 21·4 in tetragonal ceric iodate, and about 16 in a closest-packed oxygen structure.

The dimensions of the iodate group determined in ceric iodate monohydrate are compared in Table 3 with those in sodium iodate, lithium iodate, and α-iodic acid, the only other iodate compounds studied by single-crystal techniques. The neutron diffraction study of Garrett & Levy (Levy, 1954) confirms the iodine and oxygen positions reported by Rogers & Helmholz (1941) for α-iodic acid. The lithium iodate structure, based largely on powder photographs, appears to be incorrect (MacGillavry & van Eck, 1943); the sodium iodate structure of Náray-Szabó & Neugebauer (1947) also appears to be incorrect.

The Ce–O distances found in ceric iodate monohydrate are compared in Table 4 with those found in ceric oxide and in cerium oxysulfate monohydrate, the only other compounds of tetravalent cerium and oxygen which have been reported.

Thermal-decomposition studies

In view of the location of the water molecules in the unit cell, it might be expected that ceric iodate monohydrate could be dehydrated rather easily by heating. The thermobalance studies do not confirm this. They, in fact, reveal a rapid weight loss of 5·96% at about 300° C., constant weight between 300 and 380° C., and then a rapid and continuous loss of weight up to 600° C. Above 600° C. the weight is constant (CeO_2). Differential thermal analyses support these results and indicate further that the decomposition between 380 and 600° C. proceeds in at least two steps.

Qualitative analyses on the vapors obtained between 280 and 310° C. reveal the presence of hydrogen

Table 3. *Dimensions of the iodate group*

Crystal	Reference	Method	I–O	O–O
$Ce(IO_3)_4.H_2O$	This paper	X-ray, 3-dimensional Patterson and Fourier projections	1·82 Å	2·74 Å
α-HIO_3	Rogers & Helmholz (1941)	X-ray, Patterson and Fourier projections	1·80 1·81 1·89	2·75 2·78 2·78
	Garrett & Levy (Levy, 1954)	Neutron, Fourier projections	1·78 1·82 ±0·01 1·90	2·69 2·77 ±0·01 2·80
$NaIO_3$	MacGillavry & van Eck (1943)	X-ray, Fourier projections	1·80 1·80 1·83	2·65 2·81 2·81
	Náray-Szabó & Neugebauer (1947)	X-ray, variation of parameters	2·05 2·08 2·08	3·16
$LiIO_3$	Zachariasen & Barta (1931)	X-ray, powder and oscillation	2·23	3·16

Table 4. *Tetravalent cerium–oxygen distances*

Crystal	Reference	Method	Ce–O
$Ce(IO_3)_4.H_2O$	This paper	X-ray, 3-dimensional Patterson and Fourier projections	2·18 Å 2·22 2·25 2·28 2·31 2·34 2·41 2·82
CeO_2	Magnéli & Kihlborg (1951)	X-ray, powder	2·34
$CeOSO_4.H_2O$	Lundgren (1953)	X-ray, Patterson and Fourier projections	2·39 2·45 ±0·1* 2·38 2·41

* Accuracy assumed by Lundgren.

iodide as well as that of iodine. The total oxidizing power of samples between 300 and 380° C. is difficult to interpret without further information. If it is assumed, however, that no cerium is lost, that cerium remains in the tetravalent state, and that all water, either through reaction or evaporation, is lost, then the analyses indicate the approximate composition $CeI_{3\cdot8}O_{11\cdot2}$, corresponding to an average oxidation state of iodine of 4·8. It would thus appear that the water molecules, instead of being driven off, react first with iodate at about 300° C. and that phases or a phase stable up to 380° C. is left. No data are available on the reactions of even simple iodates with water at elevated temperatures, and much work of both an analytical and structural nature would need to be done before the phases or phase stable between 300 and 380° C. and corresponding to 5·96% weight loss from ceric iodate monohydrate could be characterized further.

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The Composition of an Actinolite

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A finely fibrous actinolite has been re-analysed, and the occurrence therein of a higher-than-usual water-content has been verified. This new analysis, considered in the light of recently published research, supports the view that extra hydrogen, as hydroxyl, may replace some of the oxygens in the Si_4O_{11} bands. Physical data for the re-analysed actinolite are also reported.

In a paper in a recent issue of this journal Zussman (1955) reported results of a crystal-structure study of a very finely acicular actinolite that had been collected and studied some years ago by the present writer (Hutton, 1940). The chief problem that presented itself in the earlier investigation was the large amount of water evolved above 105° C., and this appeared to lead to poor agreement with the ideal amphibole formula as proposed by Warren (1930). Zussman has now shown that there is an excess of hydrogen but not of oxygen in this particular actinolite, thus accounting for most of the high percentage of water found, and he has presented two possible ways in which such hydrogen may be accommodated in the amphibole structure. Although sufficient evidence is not available to enable him to eliminate either one or other of these alternatives he is slightly in favour of the situation in which the extra hydrogen may, as (OH) ions, replace some of the oxygens in the Si_4O_{11} bands, as occurs in afwillite, rather than that in which SiO_4 groups may be replaced by (OH), as in hydrogrossular, metamict zircon and thorite, and other silicates.

The present writer has long felt that a re-examination of this actinolite was necessary and a recent visit to New Zealand made collection of material from the original locality possible. Unaware that Zussman's investigation was under way, a new chemical analysis was made from material that was especially carefully prepared to eliminate all traces of talc and chlorite, minerals that are intimately associated with the actinolite. Accordingly, and in view of Zussman's paper, the writer would like to place this new analysis on record (Table 1, *B*) since it checks the earlier one quite closely except that a slightly lower percentage of combined water has now been determined, a fact that

Table 1. *Analyses of actinolite**

	A	*B*
SiO_2	50·21	50·47
Al_2O_3	4·55	4·18
TiO_2	1·20	1·11
Fe_2O_3	2·77	2·90
Cr_2O_3	0·10	0·08
MgO	17·85	17·94
FeO	9·03	9·20
MnO	0·19	0·14
Na_2O	0·40	0·57
CaO	9·69	9·44
K_2O	0·23	0·28
H_2O+	4·05	3·55
H_2O-	0·02	0·11
F_2	0·15	0·12
	100·44	100·09
$-O = F_2$	0·06	0·05
	100·38	100·04

Physical properties of actinolite *B*

$\alpha = 1{\cdot}630 \pm 0{\cdot}002$, $\gamma = 1{\cdot}648$; $\gamma - \alpha = 0{\cdot}018$
$2V = 69°$, $Z{:}c = 19°$

Specific gravity = 3·11 (at 18° C.)

A: Original analysis (Hutton, 1940, p. 15); 55 chains north-east of Bracken Creek–Arrow River junction, Shotover Survey District, New Zealand. Otago University Geology Department No. 2662.
B: New analysis; material from same outcrop as *A*.

* Analysis by C. Osborne Hutton.