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The Crystal Structure of Gadolinium Trichloride Hexahydrate[*]

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$GdCl_3.6\,H_2O$ is monoclinic with space group $P2/n$ and two molecules in the cell

$$a=9{\cdot}651,\ b=6{\cdot}525,\ c=7{\cdot}923\ \text{Å};\ \beta=93{\cdot}65^\circ.$$

All atomic positions (except for hydrogen) were determined with high precision.

The structure contains complexes $[Cl_2Gd(OH_2)_6]$ which are held together by $O\text{–}H\cdots Cl$ bonds. Thus one third of the chlorine atoms are not bonded to gadolinium atoms. The only symmetry element of a complex is a twofold axis. The bond lengths are:

$$\text{Gd–Cl}=2{\cdot}768,\ \text{Gd–O}=2{\cdot}39\text{–}2{\cdot}42,\ \text{O–H}\cdots\text{Cl}=3{\cdot}14\text{–}3{\cdot}24\ \text{Å}.$$

Introduction

The investigation to be reported on in the following is part of the general crystal chemical studies of 4*f* and 5*f* elements in which this laboratory has been engaged over a number of years.

The specific compound to be discussed, $GdCl_3.6\,H_2O$, is representative of an isostructure series with numerous members. It is definitely known that the corresponding compounds of neodymium, samarium, erbium (Pabst, 1931; Iveranova, Tarasova & Umanskii, 1951) and of plutonium have the same structure as $GdCl_3.6\,H_2O$, and it is probably true that most of the analogous chlorides and bromides of 4*f* and 5*f* elements, of yttrium and possibly of scandium belong to the same structure type.

Because of the ease with which large (although hygroscopic) single crystals can be prepared extensive magnetic and spectroscopic measurements have been made on many of these compounds. It is hoped that the structure results will be useful in the interpretation of these data.

Goniometric measurements have been reported (Pabst, 1931) for $GdCl_3.6\,H_2O$ and $SmCl_3.6\,H_2O$, and unit-cell dimensions have been published (Iveranova *et al.*, 1951) for the samarium and neodymium chlorides.

The single crystals used in the present investigation were furnished by Prof. G. H. Dieke of Johns Hopkins University.

$GdCl_3\ 6\,H_2O$ is monoclinic with two molecules in a unit cell of dimensions

$$a=9{\cdot}651\pm0{\cdot}001,\ b=6{\cdot}525\pm0{\cdot}001,$$
$$c=7{\cdot}923\pm0{\cdot}001\ \text{Å};\ \beta=93{\cdot}65\pm0{\cdot}02^\circ.$$

The calculated density is 2·478 g.cm.$^{-3}$. The only regular absences among the reflections are $H0L$ when $H+L$ is odd, corresponding to space group symmetry $P2/n$ or Pn.

Determination of the structure

All intensity measurements were made on a General Electric XRD-3 spectrometer rebuilt for single crystal work, using a proportional counter and filtered Cu $K\alpha$ radiation. All data were taken on one crystal which had been ground into a sphere of radius

$$2{\cdot}83\pm0{\cdot}02\times10^{-2}\ \text{cm}.$$

Since the crystals are hygroscopic, the sphere was coated with a solution of Canada balsam in benzene.

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Table 1. *Final parameters*

Atom	Position	x	y	z	B in Å^2
Gd	$2e$	$\frac{1}{4}$	0·1521 ± 2	$\frac{1}{4}$	0·72 ± 3
$\mathrm{Cl_I}$	$2f$	$\frac{3}{4}$	0·3769 ± 4	$\frac{1}{4}$	3·06 ± 11
$\mathrm{Cl_{II}}$	$4g$	0·0587 ± 4	0·8370 ± 8	0·2601 ± 4	2·92 ± 8
$\mathrm{O_I}$	$4g$	0·2813 ± 12	0·0471 ± 19	0·5432 ± 12	2·94 ± 21
$\mathrm{O_{II}}$	$4g$	0·1423 ± 12	0·4254 ± 20	0·0888 ± 12	3·24 ± 22
$\mathrm{O_{III}}$	$4g$	0·4406 ± 12	0·2988 ± 20	0·1058 ± 12	3·26 ± 22

Table 2. *Observed and calculated structure factors*

HKL	F_o	F_c	HKL	F_o	F_c	HKL	F_o	F_c	HKL	F_o	F_c
010	67	60	$21\bar{2}$	28	−22	161	50	−46	$91\bar{7}$	20	−20
$10\bar{1}$	102	96	$31\bar{1}$	38	−41	$12\bar{7}$	8	8	$27\bar{5}$	16	−13
101	103	−103	220	29	−21	027	18	17	$10,1,\bar{6}$	14	14
110	80	−66	212	21	17	426	13	14	239	9	8
011	77	−68	311	56	50	$82\bar{3}$	45	−44	182	22	22
200	91	−91	$22\bar{1}$	84	−81	260	23	−21	10,1,5	23	23
$11\bar{1}$	66	64	$10\bar{3}$	48	−49	$52\bar{6}$	34	34	817	33	31
111	69	−71	221	90	84	$80\bar{4}$	42	45	$12,1,\bar{2}$	11	−11
002	114	−134	054	21	18	$71\bar{5}$	17	−18	0,0,10	36	−37
210	42	−35	060	52	48	910	33	−33	$28\bar{2}$	16	13
$21\bar{1}$	102	−114	$30\bar{7}$	27	28	813	61	57	$80\bar{8}$	20	25
211	109	110	$15\bar{4}$	38	37	$91\bar{1}$	32	31	$15\bar{8}$	25	27
012	52	−50	236	33	−32	$22\bar{7}$	47	47	$2,0,\overline{10}$	23	25
020	40	−37	714	31	31	254	8	−6	12,1,1	28	−27
$11\bar{2}$	19	16	160	32	28	127	17	−17	058	6	6
$20\bar{2}$	61	53	615	23	22	$26\bar{1}$	14	13	$11,0,\bar{5}$	27	−30
112	40	36	154	28	28	$28\bar{1}$	38	−35	$61\bar{9}$	22	−23
120	85	−82	061	20	18	916	27	27	$1,1,\overline{10}$	19	20
$30\bar{1}$	40	−32	$31\bar{7}$	31	30	281	34	32	0,1,10	20	−21
021	24	9	$70\bar{5}$	29	−33	082	10	−10	$16\bar{7}$	19	−21
202	64	60	$16\bar{1}$	40	37	175	35	−33	067	9	−10
301	58	−43	217	42	−42	$12,1,\bar{1}$	28	28	158	21	22
$12\bar{1}$	14	−15	$25\bar{4}$	9	5	12,1,0	10	12	509	28	−31
310	71	70	822	5	4	$18\bar{2}$	23	23	083	15	19
121	68	64	$90\bar{1}$	39	44	$12,0,\bar{2}$	26	−30			

The intensities of all reflections $0KL$, $1KL$, $2KL$, $H0L$, $H1L$, $H2L$ were measured.

It was immediately evident from the experimental structure factors that the two gadolinium atoms per unit cell are in positions $\pm(\frac{1}{4}, y, \frac{1}{4})$ with $y \approx 0{\cdot}153$. These positions are compatible with either $P2/n$ or Pn. Preliminary values for the chlorine and oxygen parameters were found with the aid of ordinary and generalized Fourier difference projections on the (100) and (010) plane. In making these projections the space group symmetry $P2/n$ was assumed. Were the symmetry instead Pn, then the number of peaks due to chlorine and oxygen atoms would have been twice the number actually observed. Accordingly it was concluded that $P2/n$ was indeed the correct space group.

The final parameter values, for all but the hydrogen atoms, were obtained by least-squares refinement using the Busing–Levi (1959) program for IBM-704, and all 794 experimental structure factors. The Thomas–Umeda (1957) f-curve, corrected for anomalous dispersion (Dauben & Templeton, 1955), was used for gadolinium. For chlorine and oxygen the f-curves of Berghuis *et al.* (1955) were assumed. Isotropic temperature factors were used in the refinement. The calculations gave an R factor of 0·06 and the parameter values shown in Table 1. The degree of agreement between observed and calculated structure factors is shown in Table 2, which includes small groups of reflections with consecutive values of $\sin \theta/\lambda$ taken from the beginning, the middle and the end of the complete table of data.

Table 3. *Hydrogen positions*

Atom	x	y	z
$\mathrm{H_I}$	0·272	0·920	0·605
$\mathrm{H_{II}}$	0·364	0·082	0·608
$\mathrm{H_{III}}$	0·174	0·484	0·987
$\mathrm{H_{IV}}$	0·117	0·548	0·140
$\mathrm{H_V}$	0·534	0·322	0·149
$\mathrm{H_{VI}}$	0·476	0·258	0·002

A direct determination of the hydrogen parameters was not attempted. As will be discussed in the next section each oxygen atom has two chlorine neighbors at the distance of 3·16–3·24 Å, the angle between the two directions being 89–97°. These observations indicate strongly that the short oxygen to chlorine distances represent bonds O–H · · · Cl. If the hydrogen atoms are placed on these oxygen to chlorine connection lines and at a distance of 0·96 Å from the oxygen atom, the hydrogen parameter values of Table 3 result. The inclusion of the hydrogen atoms in the calculation does on the whole improve the agreement for reflections at small scattering angles.

Discussion of the results

It is an unexpected feature of the structure that one third of the chlorine atoms (the Cl_I-atoms) form no bonds with gadolinium atoms. Indeed, the shortest Gd–Cl_I distance is greater than 5 Å.

In the structure there are complexes $[Cl_2Gd(OH_2)_6]$, each Cl_{II} atom and each oxygen atom being bonded to one gadolinium atom. These complexes are held together by O–H · · · Cl_I and O–H · · · Cl_{II} bonds.

The configuration about gadolinium is shown in Fig. 1. The only symmetry element of the complex is a two-fold axis. The bond lengths within the complex are:

Gd–2 Cl_{II}	$2{\cdot}768 \pm 0{\cdot}008$ Å
–2 O_I	$2{\cdot}42 \pm 0{\cdot}002$
–2 O_{II}	$2{\cdot}39 \pm 0{\cdot}02$
–2 O_{III}	$2{\cdot}42 \pm 0{\cdot}02$

The closest oxygen and chlorine approaches in the complex are

$$O_I\text{–}O_{II} = 2{\cdot}80,\ Cl_{II}\text{–}O_{III} = 3{\cdot}20,\ Cl_{II}\text{–}Cl_{II} = 3{\cdot}71\ \text{Å}\ .$$

Each oxygen atom has a Cl_I atom at a distance of 3·17–3·24 Å and a Cl_{II} atom of an adjacent complex at 3·14–3·18 Å. These short distances suggest the presence of bonds O–H · · · Cl, and this interpretation is given further support by the fact that the angle between the two O–H · · · Cl bonds is 89–97°.

Conversely each Cl_I atom forms six Cl_I · · · H–O bonds and each Cl_{II} atom three Cl_{II} · · · H–O bonds in addition to the Cl_{II}-Gd bond. The individual bond distances for oxygen and chlorine atoms are listed below.

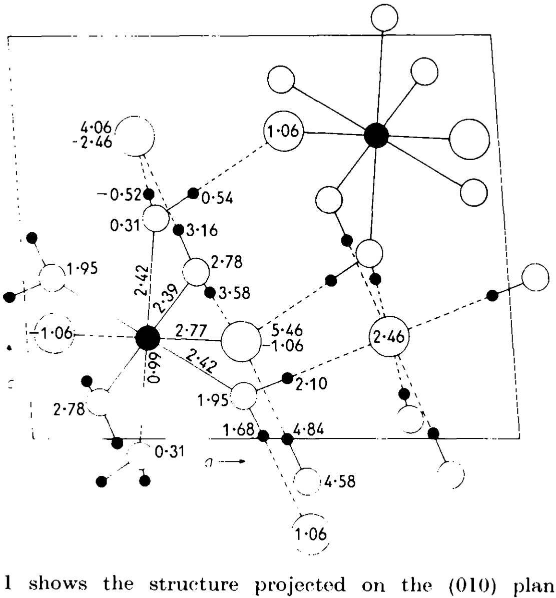

Fig. 1 shows the structure projected on the (010) plane. Large filled circles represent gadolinium atoms and small filled circles hydrogen atoms. The very large open circles are chlorine atoms and the other open circles oxygen atoms. Numbers attached to the circles give height in Å above the projection plane. The bond lengths in Å within the complex about gadolinium are also given. Only some of the hydrogen atoms have been included.

O_I–Gd	(1)	$2{\cdot}42 \pm 0{\cdot}02$ Å
O_I–H_I · · · Cl_I	(1)	$3{\cdot}24 \pm 0{\cdot}02$
O_I–H_{II} · · · Cl_{II}	(1)	$3{\cdot}18 \pm 0{\cdot}02$
∠ O_I–H_I:O_I–H_{II}		92°
O_{II}–Gd	(1)	$2{\cdot}39 \pm 0{\cdot}02$ Å
O_{II}–H_{III} · · · Cl_I	(1)	$3{\cdot}21 \pm 0{\cdot}02$
O_{II}–H_{IV} · · · Cl_{II}	(1)	$3{\cdot}14 \pm 0{\cdot}02$
∠ O_{II}–H_{III}:O_{II}–H_{IV}		97°
O_{III}–Gd		$2{\cdot}42 \pm 0{\cdot}02$ Å
O_{III}–H_V · · · Cl_I		$3{\cdot}17 \pm 0{\cdot}02$
O_{III}–H_{VI} · · · Cl_{II}		$3{\cdot}16 \pm 0{\cdot}02$
∠ O_{III}–H_V:O_{III}–H_{VI}		89°
Cl_I · · · H_I–O_I	(2)	$3{\cdot}24 \pm 0{\cdot}02$ Å
Cl_I · · · H_{III}–O_{II}	(2)	$3{\cdot}21 \pm 0{\cdot}02$
Cl_I · · · H_V–O_{III}	(2)	$3{\cdot}17 \pm 0{\cdot}02$
Cl_{II}–Gd	(1)	$2{\cdot}768 \pm 0{\cdot}008$
Cl_{II} · · · H_{II}–O_I	(1)	$3{\cdot}18 \pm 0{\cdot}02$
Cl_{II} · · · H_{IV}–O_{II}	(1)	$3{\cdot}14 \pm 0{\cdot}02$
Cl_{II} · · · H_{VI}–O_{III}	(1)	$3{\cdot}16 \pm 0{\cdot}02$

The observed bond lengths Gd–Cl and Gd–O are about 0·06–0·07 Å larger than anticipated on the basis of published ionic radii (Zachariasen, 1954). The sum of the ionic radii of chlorine and oxygen (3·27 Å) is only slightly larger than the experimental values of 3·21 Å for the O–H · · · Cl_I and of 3·16 Å for the O–H · · · Cl_{II} bonds. The Cl_I atom forms six Cl · · · H–O bonds, the Cl_{II} atom three Cl · · · H–O bonds and one Cl–Gd bond. The larger value for Cl_I · · · H–O bond is probably attributable to the larger coordination number for the Cl_I atom.

Detailed balance of valence requires a strength of about 0·8 for the O–H and 0·2 for the H · · · Cl bond.

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