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The Structure of β-Zirconium Trichloride

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The crystal structure of β-zirconium trichloride has been determined by the powder method. The hexagonal cell constants are: $a = 6.382 \pm 0.005$ and $c = 6.135 \pm 0.007$ Å. with two molecules in the unit cell. The structure is based on a distorted hexagonal close packing of chlorine atoms, with one-third of the available octahedral holes occupied by zirconium atoms, to give infinite linear chains of $ZrCl_6$ octahedra sharing opposite faces parallel to the c axis. The zirconium–chlorine distance is 2.55 Å.

Introduction

A recent publication on the crystal structure of $ZrCl_3$ by Swaroop and Flengas[1] differs greatly from the data reported almost simultaneously by Dahl, Chiang, Seabaugh, and Larsen.[2] An X-ray structural analysis in these laboratories of $ZrCl_3$ prepared by a method differing from both these groups of workers was virtually complete when these publications appeared. The results substantiate the structure reported by Dahl, and it is concluded that the structure given by Swaroop and Flengas was obtained from a particular form of zirconium trichloride exhibiting layer disorder.

Experimental Section

$ZrCl_3$ was prepared by atomic hydrogen reduction of low-hafnium $ZrCl_4$.[3] The sample of 99% purity used for the structural analysis was heated to 300° in a sealed glass ampoule for several weeks to increase the particle size, as the trichloride formed from the hydrogen reduction was very finely divided and, in most cases, gave very poor diffraction patterns. Because zirconium trihalides are extremely sensitive to moisture and oxygen, a special type of holder was designed for use with a Guinier-type focusing camera.[4] Milligram samples of $ZrCl_3$ could be safely left in it up to 24 hr. without hydrolysis.

All transfers and manipulations for the preparation of the samples were carried out in a vacuum drybox containing less than 100 p.p.m. of H_2O through which oxygen-free dried argon was continuously circulating. High purity KCl previously dried at 600° and 5×10^{-3} mm. pressure was used as an internal standard for measuring the lattice constants. The resulting X-ray diffraction data (Table I) could be indexed with a hexagonal cell of $a = 6.382 \pm 0.005$ Å. and $c = 6.135 \pm 0.007$ Å. Two molecules per unit cell gave a calculated density of 3.033 g./cc., in agreement with a measured density in a helium densitometer of 2.97 ± 0.05 g./cc. Intensity data were collected on multiple films with a 11.45-cm. Debye–Scherrer camera with samples sealed in 0.3-mm. Lindemann capillary tubes. The integrated intensities were measured on a Joyce microdensiometer, and after a scaling factor had been applied, these were compared with structure factors calculated from the relationship[5]

$$F^2 \propto I/JLpA\theta T$$

An over-all isotropic temperature factor 0.7, obtained by plotting ln (F_o/F_c) *vs.* $\sin^2 \theta/\lambda^2$, was used to bring the data into agreement over the whole range of the film.

Determination of the Structure

Systematic absences, limited to the $h0l$ reflections where l is odd, indicated possible space groups as being $P6_3mcm$, $P6_3cm$, or $P\bar{6}c2$. A comparison with the diffraction data of β-$TiCl_3$ for which the space group is $P6_3mcm$[6] indicated that these two compounds were probably isostructural, and this assumption was subsequently justified by agreement between the observed and calculated structure factors. This requires the zirconium and chlorine atoms to be in positions (2b) and (6g) with only one variable position x, in the latter to be determined. The agreement between the observed and calculated structure factors was reached by plotting x from 0.290 to 0.340 at intervals of 0.005 against the R factor where

$$R = \Sigma|F_o| - \Sigma|F_c|/\Sigma|F_o|$$

This resulted in a minimum value R of 0.17 at $x = 0.320$. Table I compares the calculated and observed data obtained. Dahl, Chiang, Seabaugh, and Larsen[2] using a similar method gave $x = 0.319$.

The basic structure of zirconium trichloride consists of chains of octahedra sharing opposite faces, parallel to the c axis. These columns of octahedra are held together only by van der Waals forces and hence zirconium trichloride should appear as fibrous needles when well-crystallized. The same type of structure has been reported from a single crystal investigation[7] of $MoBr_3$, which forms black needle-like hexagonal crystals. Furthermore, in $ZrCl_3$, there is also a distortion of the octahedra along the direction of the c axis. Thus, in the shared faces, the Cl–Cl distance is 3.53 ± 0.01 Å. and the Cl–Zr–Cl angle is 87.6 ± 0.1°, while, in the remaining faces, the Cl–Cl distances are 3.68 ± 0.01 Å. and the Cl–Zr–Cl angles are 92.0 ± 0.10°. The average Zr–Cl distance is 2.55 ± 0.01 Å. The Zr–Zr distance is 3.07 ± 0.01 Å., one-half the c axis. This distance between the Zr atoms in metallic zirconium is 3.19 Å., suggesting that the distortions of the octahedra are probably caused by metal–metal bonding between zirconium atoms. Dahl, Chiang, Seabaugh, and Larsen[2] have given a qualitative molecular orbital explanation of this metal–metal interaction occurring

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Table I

Calculated and Observed X-Ray Data

hkl	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	F_o	F_c
100	0.01941	0.01942	112.76	88.92
110	0.05829	0.05826	25.12	27.17
002	-	0.06304	< 23.91	12.07
111	0.07415	0.07412	71.30	64.35
200	0.07766	0.07768	54.70	56.80
102	0.08249	0.08246	55.92	59.31
112	0.12141	0.12130	92.60	84.93
210	0.13601	0.13594	55.40	47.03
202	0.14076	0.14072	59.20	53.56
211	-	0.15171	<12.25	7.68
300	0.17494	0.17478	98.50	104.21
212) 113)	0.19996	0.19898) 0.20010)	78.68	(50.20 (45.72
220	-	0.23304	<20.16	22.41
302	-	0.23782	<12.10	1.01
221		0.24880	<16.87	32.41
310) 004)	0.25244	0.25246) 0.25216)	76.80	(54.20 (90.70
311		0.26822	<14.70	5.33
104	0.27134	0.27158	39.21	49.53
213		0.27778	<18.14	20.16
222	0.29662	0.29608	36.60	68.80
114) 400) 312)	0.31165	0.31042) 0.31072) 0.31155)	72.69	(21.62 (50.21 (34.71
204		0.32984	<23.62	39.67
320) 402) 223)	0.37421	0.36898) 0.37376) 0.37488)	66.21	(35.19 (32.87 (36.58
321		0.38478	<17.00	6.19
214	0.38894	0.38810	42.00	39.97
313		0.39430	<16.20	4.65
410		0.40782	< 22.80	20.52
411) 304)	0.42572	0.42385) 0.42694)	82.14	(38.82 (51.60
322	-	0.43202	<26.15	16.80
115	-	0.45226	<32.71	24.12
412	0.47135	0.47086	37.06	25.71
224	-	0.48520	<18.32	22.97
500	-	0.48550	< 29.44	29.04
314	0.50437	0.50462	41.52	35.30
323	-	0.51082	<15.58	17.62
330) 215)	0.52816	0.52434) 0.52994)	36.87	(26.12 (18.02

through the overlap of metal orbitals which point along the direction of the c axis. In addition, Lewis, Machin, Newnham, and Nyholm[8] postulated that the weak magnetic moment or diamagnetism observed for ZrCl$_3$ was due to antiferromagnetic interaction resulting from metal–metal bonding which is consistent with this theory and justified on the proposed structure.

Diffuse reflectance spectra of ZrCl$_3$ reported by Clark[9] show an intense band at 17,300 cm.$^{-1}$ which was interpreted as a ligand field band $^2E_g \rightarrow T_{2g}$ transition for Zr(III) octahedrally coordinated to chloride ions. This is again consistent with the suggested structure. Spectra of our ZrCl$_3$, prepared as outlined, gave similar bands at 16,700 and 26,300 cm.$^{-1}$.

Table II

X-Ray Powder Data for ZrCl$_3$

Present study			Swaroop and Flengas(1)			Schläfer and Wille(10)		Dahl, Chiang, Seabaugh and Larsen(2)			Holze(11)	
I/I_o	hkl	d Å	I/I_o	hkl	d Å	I/I_o	d Å	I/I_o	hkl	d Å	hkl	d Å
vs	100	5.520	mw	101	4.554	sm	6.804	vs	100	5.480	001	6.172
w	110	3.190	mw	003	3.180	m	4.22	w	110) 002)	3.142	100	5.548
ms	111	2.828	s	110	2.985	m	3.29	s	111	2.817	110	3.206
mw	200	2.764	w	111	2.850	vs	2.71	wm	200	2.754	111	2.844
m	102	2.682	vs	103	2.746	s	2.31	mw	102	2.671	200	2.760
s	112	2.210	wm	004	2.404	m	2.10	s	112	2.201	102	2.696
mw	210	2.088	s	202	2.283	wm	2.01	mw	210	2.081	112	2.223
mw	202	2.053	w	203	2.014	w	1.89	m	202	2.048	210	2.098
s	300	1.841	mw	105) 212)	1.807	ms	1.82	sm	300	1.834	202	2.058
m	212) 113)	1.722	w	204	1.759	ms	1.72	m	212) 113)	1.720	300	1.850
mw	310) 004) 104)	1.523	mw	300	1.718	w	1.61	m	221) 004) 310)	1.529	212) 113)	1.732
vw	104	1.478	w	115	1.628	w	1.56	vw	104	1.477	004) 221)	1.548
w	222	1.414	w	214) 303)	1.517	w	1.49	w	222	1.412	104	1.486
w	114) 400) 312)	1.379	w	221	1.477	vw	1.45	vw	400) 312)	1.381	222	1.421
vw	320) 402)	1.259	wm	007	1.383	vw	1.34	vw	320) 402)	1.255	400	1.387
vw	411) 304)	1.180	w	400	1.291	mw	1.27	vw	214	1.234	402	1.265
vw	214	1.238	wm	305) 401)	1.261	wm	1.21	vw	410	1.202		
vvw	412	1.121	w	404	1.139	wm	1.14	vw	411) 304)	1.179		
vvw	314	1.084	wm	410	1.126			w	412	1.120		
vvw	330	1.054						vvw	224) 500)	1.103		
								vw	330	1.063		
								vvw	413	1.037		
								vvw	600	0.918		
								vvw	226	0.850		

Discussion

A detailed comparison of all the published X-ray powder patterns of ZrCl$_3$ is shown in Table II, and data characterizing the samples are shown in Table III.

The data of Holze[11] were calculated from his reported unit cell and are roughly in agreement with our data, except for the 001 reflection. In addition, this critical 001 line has not been observed in any of the other three powder patterns, and Dahl, from intensity calculations, has shown that the 001 reflection is very weak and would not account for the strong reflection observed by Holze.

In contrast to these, the powder patterns of Swaroop and Flengas[1] differ almost completely, and they have proposed a BiI$_3$ layer structure for ZrCl$_3$ based upon a subcell with a space group P$\bar{3}$m1. Their true unit cell (Table III) has metal atoms occupying any one pair of the positions

$$\text{A}\quad 0,\ 0,\ 0;\ {}^2/_3,\ {}^1/_3,\ 0$$
$$\text{B}\quad 0,\ 0,\ 0;\ {}^1/_3,\ {}^2/_3,\ 0$$
$$\text{C}\quad {}^1/_3,\ {}^2/_3,\ 0;\ {}^2/_3,\ {}^1/_3,\ 0$$

and all the chlorines in the positions

$$0,\ {}^1/_3,\ z;\ {}^2/_3,\ {}^2/_3,\ z;\ {}^1/_3,\ 0,\ z$$
$${}^1/_3,\ {}^1/_3,\ \bar{z};\ 0,\ {}^2/_3,\ \bar{z};\ {}^2/_3,\ 0,\ \bar{z}$$

with $z = 0.25$. This z parameter and the x parameter of 0.320 determined from our structure both reflect the

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TABLE III

CHARACTERIZATION OF $ZrCl_3$

Ref.	Method of prepn.	Purity, %	Density	Unit cell dimensions, Å.	
				a	*c*
[a] Present study	$ZrCl_4 + H$ 20–25° (3–4 mm.)	99	2.97	6.382 ± 0.005	6.315 ± 0.007
1	$ZrCl_4 + Zr$ 600–800° (1 atm.)	99	2.281 ± 0.075	5.961 ± 0.005	9.669 ± 0.005
2	$ZrCl_4 + Zr$ 500° (15–20 atm.)	61 (39% Zr)	2.95 ± 0.05	6.36 ± 0.01	6.14 ± 0.01
10	$ZrCl_4 + Zr$ 500° (60 atm.)	99	2.63 ± 0.10	...	...
11	$ZrCl_4 + Zr$	54 (46% Zr)	...	6.41	6.25

[a] This work.

hexagonal close packing of the chloride ions, the ideal cases giving $z = 0.25$ and $x = {}^1/_3$. Thus, the main differences between the two structures are due to the positions of the metal atoms. In our structure, the zirconium atoms are completely ordered, forming layers regularly spaced along the *c* axis at 0, 0, 0 and 0, 0, ${}^1/_2$. Swaroop and Flengas place them in layers A, B, or C, which are built up in one or other of the orders ABAB, BCBC, or CACA at random, implying a partial disorder of the zirconium atoms. The unindexed diffraction pattern of Schläfer and Wille[10] does not correspond to any of the previously discussed sets of data, except that some of the lines also appear in Swaroop and Flengas' pattern.

Since most of the analytical results give chemical formulas approaching $ZrCl_3$, the differing densities and X-ray patterns which have been reported in Table III suggest that the differences in structure and composition are due to the methods of preparation.

The extensive investigation of the structure of $TiCl_3$ by Natta, Corrandini, and Allegra[12] has suggested that it can adopt several possible types of structure. Furthermore, Reed[13] has shown from a single crystal investigation of the α form of $TiCl_3$, prepared from $TiCl_4$ and hydrogen at 800 to 900°, that it has a structure identical with that proposed by Swaroop and Flengas for their $ZrCl_3$. In addition, Reed noted diffuse reflections on his Weissenberg photographs arising from the disorder of the titanium atom layers, and this was confirmed by Natta in his independent study of α-$TiCl_3$. This supports the implied metal layer disorder suggested by Swaroop and Flengas, and, hence, their structure of $ZrCl_3$ is entirely analogous to the α form of titanium trichloride. This would further be confirmed by magnetic susceptibility measurements, which should indicate that this α form of $ZrCl_3$ is paramagnetic, similar to α-$TiCl_3$, which has a magnetic moment of 1.31 B.M.[8] at 265°K. The β form of $TiCl_3$, which is isostructural with our zirconium trichloride, is likewise weakly paramagnetic with a magnetic moment of 0.7 B.M.[8] This form can also be prepared at low temperatures by atomic hydrogen reduction of $TiCl_4$[14] in the same way as $ZrCl_3$. Furthermore, it may be suggested that there are other phases of $ZrCl_3$ similar in structure to the γ and δ forms of $TiCl_3$. These differ mainly in the mode of packing of the chlorine atoms. The γ form[13] has cubic close-packed chlorines, whereas the δ form[13] made from prolonged grinding of either α or γ has a mixture of cubic and hexagonal close-packed chlorines in disordered titanium layers.

From the foregoing discussion, it has been shown that there are two forms of zirconium trichloride: the β form, as outlined in this study, prepared under moderate or low temperatures, and the α form reported by Swaroop and Flengas, which is probably formed at higher temperatures.

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