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The Crystal Structure of Zirconyl Chloride Octahydrate and Zirconyl Bromide Octahydrate

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The compounds $ZrOCl_2.8H_2O$ and $ZrOBr_2.8H_2O$ are isomorphous and belong to the tetragonal space group D_{2d}^4–$P\bar{4}2_1c$, with $Z = 8$. For the chloride $a = 17{\cdot}08$ and $c = 7{\cdot}689$ Å, and for the bromide $a = 17{\cdot}65$ and $c = 7{\cdot}95$ Å. The zirconyl group consists of a complex in which four zirconium atoms are at the corners of a slightly distorted square and are linked along each edge of the square by two OH groups—one above and one below the plane of the square. Four water molecules are bound to each zirconium in such a manner that the arrangement of the eight oxygens about each zirconium is a distorted square antiprism. There are no zirconium–halogen bonds in the structure.

Introduction

A large number of zirconium oxyhalides have been reported in the literature (Venable, 1922). However, the only well-characterized, crystalline compounds which have been described are the zirconyl halide octahydrates, $ZrOX_2.8H_2O$. Except for goniometric measurements (Groth, 1906) and a powder photograph (Natta, 1930) of zirconyl chloride octahydrate, no crystallographic studies have yet been reported for any zirconyl halide.

A further incentive for working on the structures of these compounds is the complex, and poorly understood, aqueous chemistry of the zirconyl ion. Zirconium IV ions in solution are believed to undergo hydrolysis, polymerization, and complex formation with anions. Adolph & Pauli (1921) attempted to clarify the nature of zirconyl chloride solutions by determining conductivity, freezing point depression, chloride ion activity, and pH as functions of concentrations. To account for their results these workers postulated the existence of several complex ions; however, owing to the uncertainty in activity coefficients and the complexity of the solutions, no unique interpretation of their work seems possible at present.

Connick and co-workers have studied aqueous zirconium IV solutions by measuring the partition coefficient of Zr between the aqueous solution and a benzene solution containing a chelating agent. Connick & McVey (1949) concluded that the predominant species present in 1–2*M* perchloric acid are Zr^{+4} and $ZrOH^{+3}$ if the zirconium concentration is less than $10^{-4}M$, and that these ions readily form complexes with a large number of anions, including halides. Connick & Reas (1951) investigated the polymerization of zirconium species in solutions of zirconium perchlorate in aqueous perchloric acid. These workers demonstrated that appreciable polymerization occurs in 1–2*M* acid above a zirconium IV concentration of about $2 \times 10^{-4}M$. They concluded that a continuous series of polymers exists, the average degree of polymerization reaching very high values in concentrated solutions. On the other hand, Kraus & Johnson (1953) have carried out ultracentrifuge studies of various zirconyl solutions and report degrees of polymerization from 2 to 5·4 but find no evidence for high polymers.

It was our hope that a study of the crystal structures of zirconyl halides would shed some light on this polymerization problem as well as to indicate the probable coordination number of zirconium IV in aqueous solution.

Experimental

Low-hafnium $ZrOCl_2.8H_2O$ was given to us by the Titanium Alloy Manufacturing Division of the National Lead Company. Suitable crystals of the chloride were obtained by recrystallization of this material from HCl solutions, and the bromide crystals were prepared by several recrystallizations from aqueous HBr. The crystals were thin prisms, the prism axis being [001]. They effloresce on exposure to air, and we found it necessary to place them in capillaries in order to obtain suitable diffraction data. Preliminary Weissenberg photographs showed the crystals to be tetragonal, and unit-cell parameters of the chloride, obtained from oscillation photographs, are

$$a = 17{\cdot}08 \pm 0{\cdot}02, \quad c = 7{\cdot}69 \pm 0{\cdot}01 \text{ Å} .$$

The dimensions of the bromide cell, obtained from layer-line measurements and a Weissenberg photograph of a crystal rotated about [001], are

$$a = 17{\cdot}65 \pm 0{\cdot}1, \quad c = 7{\cdot}95 \pm 0{\cdot}1 \text{ Å} .$$

The density of the chloride was determined by the flotation method to be 1·965 g.cm.$^{-3}$. There are therefore 8 formula units of $ZrOCl_2.8H_2O$ per unit cell (8·2 calculated). These unit-cell data are in agreement

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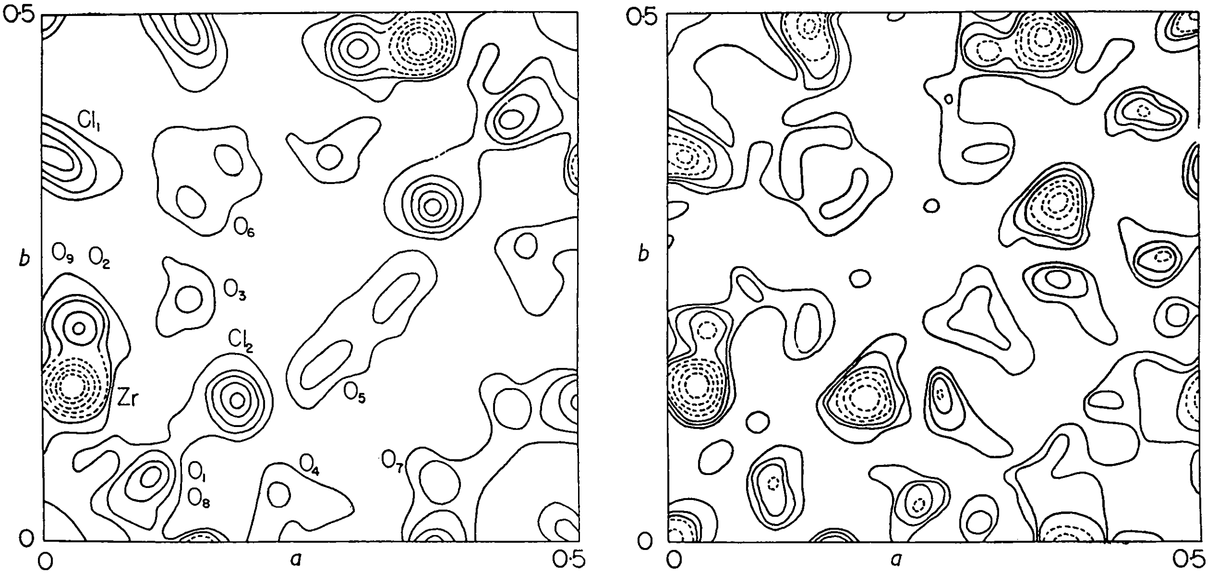

(a) (b)

Fig. 1. (a) Electron density of $ZrOCl_2.8H_2O$ projected along [001]. Solid contours are at intervals of 4 e.Å^{-2}. Broken contours are at intervals of 12 e.Å^{-2}. (b) Electron density of $ZrOBr_2.8H_2O$ projected along [001]. Contours are at an arbitrary interval.

with the axial ratio given by Groth (1906), although the latter corresponds to a non-primitive cell with edges $\mathbf{a}+\mathbf{b}$ and $\mathbf{a}-\mathbf{b}$.

The systematic absences are (hhl) when l is odd and ($h00$) when h is odd. If we assume that these absences are due to glide components, the space group is unambiguously established as D_{2d}^4–$P\bar{4}2_1c$.

The diffraction maxima for the ($hh0$) and ($h0l$) reflections of the chloride, and the ($hk0$) and ($hk1$) reflections of the bromide, were obtained with a Weissenberg camera and with Cu $K\alpha$ radiation. Intensities were measured by visual comparison with an intensity strip and converted to relative $|F|^2$'s.

Structure determination

Patterson projections on (001) and (010) were first computed for the chloride. From the former it was possible to find approximate x and y coordinates for the zirconium and chlorine atoms, which are in general (eightfold) positions. On the (010) projection, the principle maxima had z parameters of 0 or $\frac{1}{2}$, and there was an approximate center of symmetry at $x = \frac{1}{4}$, $z = \frac{1}{4}$ (or, in other words, a pseudo lattice-point at $x = \frac{1}{2}$, $z = \frac{1}{2}$). This corresponds to the fact, which was obvious on inspection of the photograph, that the ($h0l$) reflections are relatively weak for $h+l$ odd. It was apparent that z parameters for the zirconium atom could be taken as zero and we also interpreted the projection in terms of a structure in which the z coordinates for the halogens were also zero.

Fourier projections on (001) and (010) were then computed on the basis of these trial positions for zirconium and chlorine. This structure, of course, predicts $F = 0$ for ($h0l$) reflections with $h+l$ odd, and the (010) Fourier showed a false lattice point at $x = \frac{1}{2}$, $z = \frac{1}{2}$. The (001) projection was satisfactory—there were peaks of the correct relative heights in the assumed positions. On the other hand, it appeared from examination of the (010) projection that we had assumed incorrect z values for the halogen atoms. It was clear that z for Cl_2 should be about $\frac{1}{2}$ instead of zero, but the location of Cl_1 was not apparent.

At this stage of the investigation we decided to use the data obtained with the isomorphous compound $ZrOBr_2.H_2O$ to place the trial structure on a firmer basis as well as to find the z coordinate for Cl_1. The Patterson projection and the Fourier projection (Fig. 1(b)) on (001) showed complete agreement with our x and y coordinates for zirconium and halogens. To find approximate z values, we used the ($hk1$) data and the method of generalized Patterson and Fourier projections (Dyer, 1951; Cochran & Dyer, 1952). This method has the important advantage that the shortest projection is used and excessive overlapping of peaks is avoided. On the other hand, z parameters obtained by this method are rather inaccurate since only ($hk1$) data are used. However, this proved to be a satisfactory method for finding the trial structure; additional refinement of z parameters was achieved with ($h0l$) data. Analysis of the Patterson function showed clearly that the z coordinate of Br_1 is between $\frac{1}{4}$ and $\frac{1}{2}$ ($\frac{3}{8}$ assumed) and that of Br_2 is close to $\frac{1}{2}$. On the basis of these coordinates and previous x and y coordinates, phase angles were calculated and the generalized projection $\varrho_1(x, y)$ was computed:

$$\varrho_1(x, y) = \int_0^1 \varrho(x, y, z) \exp[-2\pi i z]\, dz$$
$$= \frac{1}{A_{xy}} \sum_{h,k} F_{hk1} \exp[2\pi i(hx+ky)]\,.$$

The z coordinate of Br_1 was estimated from this function to be 0·385. Peaks at the correct x coordinates and $z = 0{\cdot}368$ were found on $\varrho(x, z)$ for $ZrOCl_2.8H_2O$ and, because of good agreement with the generalized projection for the bromide, it was assumed that they were Cl_1 (see Fig. 2(*a*)).

The next task was to locate the oxygen atoms. On careful inspection of the (001) projection for both the chloride and bromide, we found seven smaller peaks which we thought were probably oxygen atoms. After considering several other possibilities, we decided that the two largest of these peaks corresponded to superposition of two oxygen atoms with nearly the same x and y coordinates. With this assignment, it is clear that the coordination of oxygen atoms about each zirconium is a square antiprism. This interpretation is consistent with the (010) projection. The first z coordinates for oxygen atoms were obtained by assuming reasonable Zr–O, O–O, and Cl–O distances. Refinement of parameters was carried out by Fourier projections on (001) and (010) for $ZrOCl_2.8H_2O$ (Figs. 1(*a*) and 2(*a*)). Final parameters were obtained from difference syntheses in which only Zr and Cl were used in F_c (Fig. 2(*b*)). The final atomic positions are given in Table 1 and the structure is illustrated in Fig. 3.

Table 1. *Atomic positions in* $ZrOCl_2.8H_2O$ *and* $ZrOBr_2.8H_2O$

	x	y	z
	$ZrOCl_2.8H_2O$		
Zr	0·029	0·145	0·001
Cl_1	0·006	0·361	0·364
Cl_2	0·185	0·134	0·488
O_1	0·098	0·061	0·161
O_2	0·037	0·201	0·719
O_3	0·136	0·209	0·993
O_4	0·240	0·048	0·007
O_5	0·283	0·180	0·820
O_6	0·132	0·321	0·591
O_7	0·361	0·060	0·218
O_8	0·097	0·059	0·816
O_9	0·036	0·201	0·282
	$ZrOBr_2.8H_2O$		
Zr	0·028	0·147	0·00
Br_1	0·011	0·365	0·38
Br_2	0·187	0·134	0·50

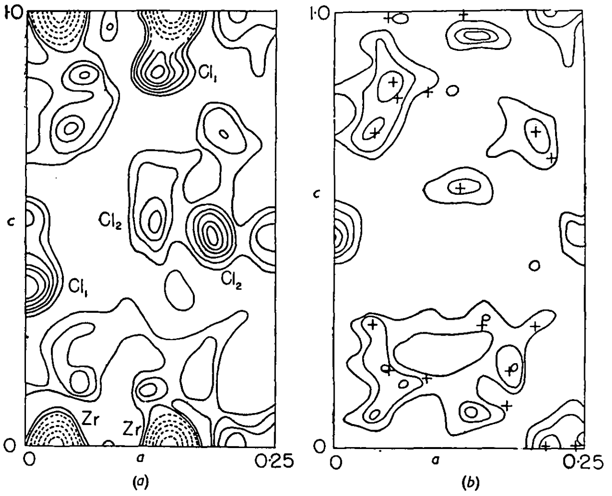

Fig. 2. (*a*) Electron density of $ZrOCl_2.8H_2O$ projected along [010]. Solid contours are at intervals of 4 e.Å^{-2}. Broken contours are at intervals of 16 e.Å^{-2}. The lowest contour is 8 e.Å^{-2}.

(*b*) Difference ($F_o - F_c$) Fourier projection of $ZrOCl_2.8H_2O$ along [010]. Only zirconium and chlorine used in F_c. Contours are at intervals of 4 e.Å^{-2}. The lowest contour is at 8 e.Å^{-2}. Crosses mark positions of oxygen atoms in final structure.

No refinement was made for $ZrOBr_2.8H_2O$, and signs of the structure factors which were used to compute the Fourier projections (Fig. 1(*b*)) for this compound were determined entirely from the zirconium and bromine positions.

For the final parameters of $ZrOCl_2.8H_2O$, $R = 0{\cdot}256$ for the ($hk0$) reflections, and 0·291 for the ($h0l$) reflections. Part of this discrepancy undoubtedly arises from absorption errors and also, probably, from incomplete refinement, particularly for the ($h0l$) data. There may also be some disorder in the structure: the shape of the Cl_1 peak on the (001) projection is extremely anisotropic, and on the (010) projection there is a peak close to Cl_1 (at $x = 0$, $z = 0{\cdot}461$) which may be due to some uncertainty in the location of this atom. For $ZrOBr_2.8H_2O$, $R = 0{\cdot}376$ for the ($hk0$) data and $R = 0{\cdot}316$ for the (hkl) reflections. The

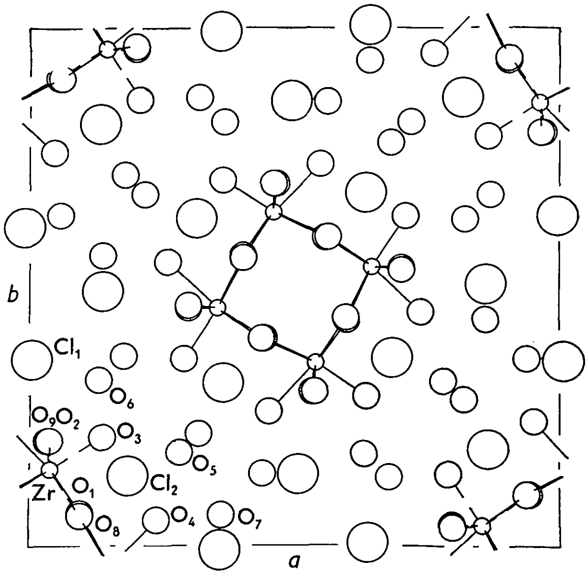

Fig. 3. Projection of one unit cell of $ZrOCl_2.8H_2O$ (and $ZrOBr_2.8H_2O$) on (001). Bonds in the $[Zr_4(OH)_8.16H_2O]^{+8}$ ion are shown as solid lines.

oxygen atoms were not used in computing structure factors for this compound.

Discussion

A list of the Zr–O distances, and the O- -O and O- - -Cl distances less than 3·5 Å, is given in Table 2.

Table 2. *Interatomic distances in* $ZrOCl_2.8H_2O$

$Zr–O_1$,	= 2·23 Å	$Zr–O_2$	= 2·37 Å
$Zr–O_1'$,	= 2·13	$Zr–O_3$	= 2·13
$Zr–O_8$,	= 2·35	$Zr–O_4$	= 2·09
$Zr–O_8'$,	= 2·22	$Zr–O_9$	= 2·37
O_2- -O_6	= 2·79	O_4- -O_5	= 2·77
O_3- -O_5	= 2·88	O_4- -O_7	= 2·64
O_3- -O_6	= 2·91	O_5- -O_7	= 2·88
Cl_1- -O_2	= 3·42	Cl_2- -O_2'	= 3·34
Cl_1- -O_6	= 2·85	Cl_2- -O_5	= 3·15
Cl_1- -O_7	= 2·89	Cl_2- -O_5'	= 3·00
Cl_1- -O_7'	= 3·41	Cl_2- -O_6	= 3·41
Cl_1- -O_9	= 2·85	Cl_2- -O_8	= 3·20
Cl_2- -O_1	= 3·18	Cl_2- -O_9	= 3·21
Cl_2- -O_2	= 3·29	Cl_2- -O_9'	= 3·41

Although the zirconium positions are fairly accurate, it is evident that there may be errors as large as 0·2 Å in the positions of the oxygen atoms. It is clear, however, that in these compounds the zirconyl species is a complex, $[Zr_4(OH)_8.16H_2O]^{+8}$, in which the zirconium atoms are arranged in a square and are linked along each edge of the square by a pair of OH groups —one above and the other below the Zr plane. The fact that these linking oxygens each have only one near neighbor—a chloride ion—is evidence that they are actually OH groups. There are four additional water molecules bound to each Zr atom in such a way as to produce a distorted square antiprism. The remaining water molecules and the chloride ions form a matrix which holds the zirconyl complexes together. It does not seem possible, with the present data, to assign unique orientations to all of the water molecules.

The variability of the Zr–O distances undoubtedly is caused by inaccuracies in the oxygen positions. The average of the Zr–O distances is 2·24 Å; the sum of the ionic radii is 2·20 Å (Pauling, 1945).

An important question arises concerning the possibility of drawing conclusions about the nature of solutions of zirconyl compounds from this structure determination. Namely, is the $[Zr_4(OH)_8.16H_2O]^{+8}$ ion an important species in aqueous solution? And why is the activity of chloride ion so low in zirconyl chloride solutions? We believe that the evidence favors the existence of this ion in solution. It is an obvious fact that it is a stable species in the solid hydrate; it is also true that its weight falls within the range reported by Kraus & Johnson (1953). Additional evidence against the formation, in acid solutions, of polymer species containing hundreds of zirconium atoms, as reported by Connick & Reas (1951), is found in our viscosity measurements of zirconyl chloride solutions in 2 molar HCl. The specific viscosity of these solutions is low; at concentrations up to 0·077 molar it is less than 0·05. These low viscosities indicate that there are no large linear or plate-like polymers in these solutions. On the other hand, formation of large, compact networks would probably result in precipitation.

It does not seem likely that the low activity of chloride ion in solution of zirconyl chloride solution is due to formation of specific complexes in which there are Zr–Cl bonds. On the other hand, a highly-charged $[Zr_4(OH)_8.16H_2O]^{+8}$ ion would certainly exert a strong attractive force on any negative ion. The formation of multiple-ions of an electrostatic nature seems very probable.

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