$PF_2OC\equiv$ skeleton is varied from 0 to 3 is now known, as is the series of adducts, excluding the adduct of PF_2O-*t*-Bu. The basicity order of the series[24] predicts the electron-releasing order *i*-Pr > Et > Me. This order is in agreement with previous work[1] and with the classical electron-releasing ability.[18-23]

The effect of substituting a methyl group for a hydrogen upon the basicity of these difluorophosphites is additive. A plot of the number of attached methyls *vs.* J_{PB} is linear. The relationship of J_{PB} *vs.* the number of attached methyls can be used to predict a J_{PB} coupling constant for PF_2O-*t*-Bu·BH_3 of 74.7 Hz. See Figure 1.

Foester and Cohn[5] have reported that a 1:1 correlation between displacement base strength and J_{PB} is not possible in a series of the type PF_2X (X = Me, MeO, Me_2N, MeS). However, Rudolph and Schultz[4] indicated that for a series of smoothly varying phosphine ligands [*i.e.*, PF_2X (X = F, Cl, Br) or $PF_{3-n}H_n$] the relationship between the magnitude of J_{PB} and the dative bond strength is a general one. The relationship between J_{PB} and the displacement base strength of the smooth series $PF_2OC(CH_3)_{3-n}H_n$ is essentially quantitative. See Table III.

Table III

Ligand	Adduct J_{PB}, Hz	ΔJ_{PB}, Hz	Av % displacement[a]	Δ(av % displacement)[b]
PF_2O-*i*-Pr	72.5			
		2.1	60.5	10.5
PF_2OEt	70.4[c]			
		2.2	60.5[c]	10.5
PF_2OMe	68.2[d]			

[a] See Table I. Average per cent displacement is calculated by averaging the two per cent displacements obtained from the pairs of exchange reactions. [b] Change in per cent displacement is calculated by subtracting 50% from the average per cent displacement. Per cent displacement for the reaction $PF_2OEt + PF_2OEt\cdot BH_3 \rightleftarrows PF_2OEt + PF_2OEt\cdot BH_3$ is 50% (K_{eq} = 1). See Table I. [c] See ref 1. [d] See ref 3.

Verkade and White[5] have recently correlated the relative stability of borane adducts with BH stretching frequencies. Coyle and Stone[26] originally suggested that BH ir stretching frequencies could be related to boron-ligand bond strength in boron adducts, but Cohn[5] found no simple relationships in a series of similar fluorophosphine-boranes. Although the differences in frequencies (cm^{-1}) are small in the series PF_2OR [R = *i*-Pr (2438, 2378), Et (2448, 2382),[1] Me (2452, 2383),[1] Tfet (2456, 2382)[1]], a trend similar to that suggested by Coyle and Stone and demonstrated by Verkade and White is evident.

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Registry No. PF_2O-*t*-Bu, 41380-08-9; PF_2O-*i*-Pr, 1737-83-3; PF_2O-*i*-Pr·BH_3, 41380-10-3; B_2H_6, 19287-45-7.

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[24] Steric effects on the basicity are assumed to be small in relation to (p-d)π electron drift from the oxygen system since the order of basicity is not that expected for steric requirements, $PF_2OMe > PF_2OEt > PF_2O$-*i*-Pr. See ref 1, 3, and 5. See also H. C. Brown, *J. Amer. Chem. Soc.*, **75**, 16 (1953).

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Characterization of the Thermal Dehydration of Zirconium Oxide Halide Octahydrates

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The compounds $ZrOX_2\cdot 8H_2O$ (X = Cl, Br) dehydrate thermally in a stepwise manner to the respective hexahydrates, tetrahydrates, and finally ZrO_2. Dehydration is complete at 700°. The intermediate hydrates have been isolated and characterized. Several regions of the infrared spectra of the various hydrates have been assigned with the aid of analogous deuterated compounds. The experimental evidence may be interpreted in terms of the structural formulations $[Zr_4(OH)_8(H_2O)_{16}]X_8\cdot 12H_2O$, $[Zr_4(OH)_8(H_2O)_{16}]X_8\cdot 4H_2O$, and $[Zr_4(OH)_8(H_2O)_{12}]X_8$, for the octahydrates, hexahydrates, and tetrahydrates, respectively. The last tetrameric cation is proposed to contain seven-coordinate Zr(IV).

Constant-temperature dehydration of zirconium oxide chloride octahydrate, $ZrOCl_2\cdot 8H_2O$, at varying humidities has been investigated previously.[1,2] The inconsistencies among the results reported in these studies are indicative of the difficulty of establishing equilibrium in the experimental system. Furthermore, dynamic thermal dehydration studies have employed rapid heating rates on bulk samples in stagnant atmospheres and have produced varying results.[3,4] We undertook the present investigation with the principal objective of clarifying the thermal behavior of the octahydrates of both $ZrOCl_2$ and $ZrOBr_2$.

X-Ray crystallographic studies have shown[5,6] that the correct structural formulation of $ZrOCl_2\cdot 8H_2O$ is $[Zr_4(OH)_8$-

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[1] T. P. Spasibenko and S. A. Kobycheva, *Russ. J. Inorg. Chem.*, **15**, 181 (1970).

[2] W. A. Castor, Jr., and F. Basolo, *J. Amer. Chem. Soc.*, **75**, 4804 (1953).

[3] (a) S. Takagi, *J. Chem. Soc. Jap.*, **75**, 637 (1954); *Chem. Abstr.*, **49**, 765*i* (1954); (b) J. H. Canterford and R. Colton, "Halides of the Second and Third Row Transition Metals," Wiley, London, 1968, p 132.

[4] L. N. Komissarova, V. E. Plyuschehev, and I. N. Kremenskaya, *Russ. J. Inorg. Chem.*, **5**, 281 (1960).

[5] A. Clearfield and P. A. Vaughan, *Acta Crystallogr.*, **9**, 555 (1956).

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$(H_2O)_{16}]Cl_8 \cdot 12H_2O$. In the tetrameric complex cation the four Zr(IV) atoms form a slightly distorted square arrangement held together by dihydroxo bridges. Four H_2O molecules are bound to each Zr(IV) to complete a distorted dodecahedral, eight-coordinate geometry.[6] The fact that $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 12H_2O$ is one of the very few structurally well-characterized compounds containing both lattice and coordinated H_2O, as well as bridging OH^-, prompted us to carry out parallel infrared spectroscopic studies with the intent of locating the characteristic vibrational modes of these three components of many hydrated solids.

Experimental Section

Zirconium oxide chloride octahydrate was prepared from reagent grade zirconium tetrachloride (Alfa) according to the procedure of Brauer.[7] The material was recrystallized three times from 1 *N* hydrochloric acid. Since solutions of zirconium oxide chloride octahydrate readily supersaturate, recrystallization was greatly speeded by addition of seed crystals. Crystals used in the study were white, well-separated needles about 0.5 cm in length. Clumps and mats of poorly separated crystals were found to give irreproducible results. $ZrOCl_2 \cdot 8H_2O$ effloresces significantly only in dry air. The crystals could be collected without decomposition by suction filtration. The material was best washed with an ice-cold mixture of equal volumes of ethanol and concentrated hydrochloric acid. Washing with acetone, pure ethanol, or ether results in serious decomposition of the crystals. The compound was found to be free of ferric ion when tested with potassium thiocyanate solution. *Anal.* Calcd: Zr, 28.30; Cl, 22.00. Found: Zr, 28.46; Cl, 22.22. The crystals were further characterized by their X-ray powder diffraction pattern which showed a tetragonal unit cell of dimensions $a = 17.11 \pm 0.02$ and $c = 7.71 \pm 0.02$ Å, in good agreement with published results.[5,6]

The deuterio analog was prepared by a similar procedure using 99.8% D_2O (Columbia) and gaseous DCl (Merck). Rapid exchange of D_2O with atmospheric water made recovery of a perfectly deuterated compound impossible. Infrared spectra indicated the product was about 80% deuterated.

Zirconium oxide bromide octahydrate was prepared by dissolving 10 g of zirconium tetrachloride in 25 ml of iced water. Seventy-five milliliters of concentrated hydrobromic acid (Allied) was added to precipitate the crude product. This product was collected, redissolved, and reprecipitated three times to eliminate chloride ion. The material was dissolved in 15 ml of water containing 2 ml of concentrated hydrobromic acid. The solution was concentrated at 70° until crystallization began. The compound was recrystallized three times. As in the case of $ZrOCl_2 \cdot 8H_2O$, seeding the solutions increased the rate of recrystallization significantly. White, well-separated needles 0.5 cm in length were selected and washed by decantation with an ice-cold mixture of equal volumes of ethanol and hydrobromic acid. Zirconium oxide bromide octahydrate effloresces somewhat even in room air. The crystals were picked from the wash, quickly pressed between absorbent filter paper, and then bottled. The compound was found to be free of ferric ion when tested with potassium thiocyanate solution. *Anal.* Calcd: Zr, 22.19; Br, 38.87. Found: Zr, 22.19; Br, 39.11; Cl, <0.1. X-Ray powder diffraction patterns indicated a tetragonal unit cell of dimensions $a = 17.67 \pm 0.04$ and $c = 7.97 \pm 0.04$ Å, in accord with published results.[5,6]

Zirconium oxide chloride tetrahydrate, zirconium oxide bromide tetrahydrate, and **zirconium oxide chloride tetradeuterate** were prepared by keeping the respective octahydrate or octadeuterate in a 200-μ vacuum for 24 hr at room temperature. Exchange between D_2O in the tetradeuterate and atmospheric water was slow and a well-deuterated species was easily collected. *Anal.* Calcd for $ZrOCl_2 \cdot 4H_2O$: Zr, 35.34; Cl, 27.50. Found: Zr, 35.78; Cl, 27.62. Calcd for $ZrOBr_2 \cdot 4H_2O$: Zr, 26.90; Br, 47.20. Found: Zr, 27.12; Br, 47.34. X-Ray powder diffraction patterns of the tetrahydrates were of poorer quality than those of the octahydrates and exhibited some background fogging. The *d* spacings for the discernible lines of $ZrOCl_2 \cdot 4H_2O$ are (relative intensities are given in parentheses) 6.55 (5), 3.73 (6), 3.59 (10), 3.38 (6), 3.09 (6), 2.84 (4), 2.75 (4), 2.14 (10), 2.06 (8), 1.72 (8), and 1.56 Å (4). The *d* spacings for $ZrOBr_2 \cdot 4H_2O$ are 7.02 (5), 4.31 (6), 4.03 (8), 3.88 (5), 3.69 (5), 3.33 (8), 2.84 (10), and 2.76 Å (6).

Zirconium oxide chloride hexahydrate and **zirconium oxide bromide hexahydrates** were prepared by controlled thermal dehydration of the respective octahydrates in an atmosphere of moist helium in the thermogravimetric apparatus described below. The hexahydrates gave poor X-ray powder patterns with much background fogging. The *d* spacings for discernible lines in the chloride are 6.78 (8), 4.67 (4), 3.53 (2), 3.18 (10), 2.37 (4), 2.15 (2), 1.79 (6), and 1.70 Å (4). For the bromide they are 3.96 (8), 3.78 (6), 3.65 (2), 3.51 (8), 3.18 (10), 2.64 (2), and 2.10 Å (2).

Differential thermal analysis (dta) was carried out with a Du Pont Model 900 differential thermal analyzer over the temperature range of 23–450°. Heating rates of 20, 15, and 5° min^{-1} were used. Resolution of the thermograms was greater at the lower heating rates.

Thermogravimetric analysis (tga) was performed using a Du Pont Model 950 thermogravimetric analyzer attachment to the above dta. Analyses were done in a flowing atmosphere of dry or moist helium at a heating rate of 1° min^{-1}. Higher heating rates reduced the quality of the thermograms. Samples of about 20 mg were used. Larger or smaller samples did not significantly affect the thermograms. Changes in the rate of flow of the atmosphere around the samples affected the quality of the thermograms. A relatively high, constant flow rate of 500 cm^3 min^{-1} was used throughout the study.

Effluent gas from the tga was analyzed by bubbling it through reagent solutions. The gas would not reduce iodide in 0.1 *N* KI solution and must have been free of elemental halogen. It proved to be free of Zr(IV) when tested with alizarin.[8] The effluent gas would precipitate silver halide from 0.05 *N* silver nitrate solution. These precipitates were measured gravimetrically.

Dehydration in moist helium, prepared by bubbling the gas through a gas scrubbing tower filled with room-temperature water, was carried out over the range 23–200°. Thermal dehydration in dry helium was continued to at least 700°.

Crystals used in tga were not crushed. A minimum of grinding was used to prepare samples for dta. This was found necessary to obtain sharp transitions in the thermograms. Similar procedures have been found necessary in the thermal analysis of organic hydrates.[9]

Temperatures at which phase transformations are reported from dta thermograms are higher than those taken from tga thermograms because of the experimental arrangements. Samples in dta were confined in 1.0-mm diameter tubes in a stagnant atmosphere. In tga the samples were held in open pans surrounded by a flowing atmosphere.

Infrared spectra over the region 4000–200 cm^{-1} were recorded on a Perkin-Elmer Model 225 spectrophotometer. The instrument was calibrated against known lines in the water vapor spectrum. Hydrates were run in disks of CsI and KBr as well as Nujol mulls. Better resolution, especially in the high-energy region of the spectrum, was obtained in the spectra of the disks. Deuterates were run as Nujol mulls. The 800–700-cm^{-1} region was also examined in KBr disks. Spectra were taken at 303 and 93°K. Low-temperature spectra were obtained with the sample mounted in a Research and Industrial Instrument Co. VLT-2 dewar equipped with CsI windows.

X-Ray powder patterns were obtained using a 114.6-mm Debye-Scherrer camera with film mounted in the Stramanis arrangement. Samples were mounted in 0.2-mm Glaskapillern tubes and subjected to rotation and reciprocation during irradiation. Iron-filtered cobalt Kα radiation was used.

Results

Differential thermograms of $ZrOCl_2 \cdot 8H_2O$ and the isomorphous bromide are shown in Figure 1. The thermogram of the chloride shows a weak, broad, endothermic band, centered at 35°. Such a band at this low temperature is indicative of the loss of weakly held material from the crystal lattice with little change in structure. A sharp, but still weak, endothermic band appears at 82°. These weak bands are well separated from a complex series of strong, endothermic peaks between 105 and 140°. Band maxima in this envelope of strong bands are at 109, 117, 130, and 135°. Above 140° no significant bands can be detected in the chloride, although thermal dissociation obviously continues.

The thermogram of $ZrOBr_2 \cdot 8H_2O$ is similar, with weak, en-

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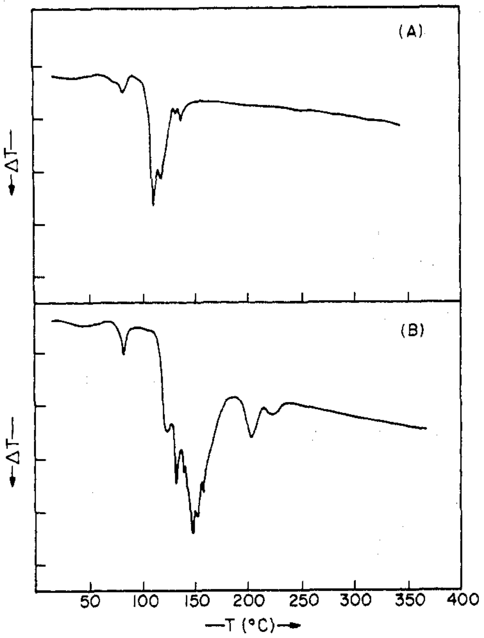

Figure 1. Differential thermograms of (A) $ZrOCl_2 \cdot 8H_2O$ and (B) $ZrOBr_2 \cdot 8H_2O$.

dothermic bands at 45 and 82°, and a complex series of strong peaks at 133, 148, 153, 157, and 162°. The strong bands are more numerous and better resolved than for the chloride. In addition, there are two strong, broad peaks at 218 and 235°. No corresponding peaks were detected in the thermogram of the chloride. The multiple peaks in the differential thermograms above 100° were completely reproducible and could not be due to mechanical changes in the sample during the course of thermal analysis.

The thermograms of the hexahydrates are similar to those of the octahydrates with the band at the lowest temperature absent. The thermograms of the tetrahydrates exhibit no bands below 95°, but otherwise they are identical with those for the octahydrates.

The many phases reported[1,2] for the isothermal dehydration of $ZrOCl_2 \cdot 8H_2O$ were not observed in the thermal dehydration of the compound nor of the isomorphous bromide. It is apparent that samples which undergo considerable alteration yield dubious results in constant-temperature dehydration[10] and the appearance of stoichiometric phases therefore is much more reliably observed by thermal dehydration. Thermal dehydration in a flowing, dry atmosphere also circumvents the problem of water absorption which invalidates many isothermal studies.

Nevertheless, previous reports of thermal dehydration of the $ZrOX_2 \cdot 8H_2O$ compounds are contradictory as well as being in disagreement with our results. Takagi specifically stated[3] that there are no intermediate phases in the dehydration of $ZrOCl_2 \cdot 8H_2O$ to zirconium oxide and that dehydration is complete at 180°. Komissarova, *et al.*, reported[4] that 3 equiv of water is lost at 40° and the remaining step of the dehydration processes involves simultaneous loss of water and "Cl_2." In the case of $ZrOBr_2 \cdot 8H_2O$, Takagi[11] reported a hexahydrate at 75° and a trihydrate at 125°. In both of these investigations bulk samples were used in stagnant atmospheres with heating rates of at least 10° min^{-1}.

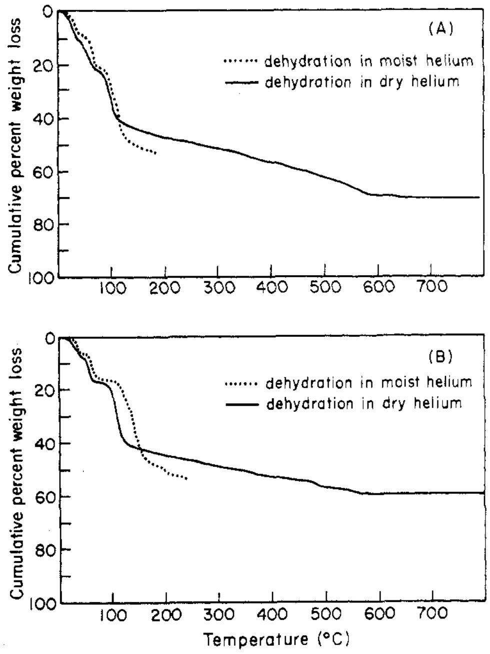

Figure 2. Thermal gravimetric traces of (A) $ZrOCl_2 \cdot 8H_2O$ and (B) $ZrOBr_2 \cdot 8H_2O$. Analyses done in dry helium are indicated by the solid line; those done in moist helium, by the dotted line.

The thermogravimetric traces for $ZrOCl_2 \cdot 8H_2O$ and $ZrOBr_2 \cdot 8H_2O$ are shown in Figure 2. The temperatures at which each step of the dehydration is complete and the cumulative per cent weight losses are given in Table I. Quantitative data presented represent averages for several dehydrations, and deviations among individual analyses are indicated by the error limits associated with the values.

The dehydration proceeds in four steps for both compounds. In each case the first and second steps involve the loss of 2 equiv of water. These steps are well separated from the subsequent and more complex steps. The third step of the dehydration of the chloride involves the loss of 2 equiv of water and 1 equiv of hydrogen chloride. For the bromide this step more closely fits the loss of 1 equiv of water and 1 equiv of hydrogen bromide. This difference in the third dehydration step is also reflected in the differential thermograms for the bromide and the chloride. In moist atmosphere this third dehydration step is accelerated and corresponds to the loss of 1 equiv of hydrogen bromide and slightly more than 2 equiv of water. After the third step there ensues a period of slow loss of hydrogen halide and the remaining water from both compounds. No stoichiometric phases could be detected in this region of the thermogravimetric trace. In particular, we have found no evidence for the dihydrate reported by Kharitonov and Zaitsev.[12] The slow loss of water and hydrogen halide above 140° considerably complicates the estimation of the completion of the third step of the dehydration. The results listed in Table I, therefore, probably do not refer to a stoichiometric phase.

Figure 3 shows that hydrogen halide is lost rapidly in the temperature range 80-120° and more slowly between 120 and 600°. The sharp weight loss at about 500° seems to be primarily attributable to halide removal. The final product of the dehydration of both the chloride and the bromide was identified by its infrared spectrum and X-ray powder diffraction pattern as ZrO_2 (baddeleyite). A constant-weight prod-

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(10) E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).

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(12) Yu. Ya. Kharitonov and L. M. Zaitsev, *Russ. J. Inorg. Chem.*, **13**, 476 (1968).

Table I. Dehydration of Zirconium Oxide Halide Octahydrates

Temp at which dehydration step is complete, °C	Cumulative % wt loss	Theoret cumulative % wt loss for the indicated loss	Type of loss
	$ZrOCl_2 \cdot 8H_2O$ in Dry Helium		
46 ± 2	11.0 ± 1.0	11.2	Loss of 2 H_2O
77 ± 4	22.5 ± 0.2	22.4	Loss of 4 H_2O
117 ± 2	42.2 ± 1.0	44.8	Loss of 6 H_2O + 1 HCl
512 ± 12		(No assignment)	
650	69.5 ± 0.2	70.0	Dehydration to ZrO_2
	$ZrOCl_2 \cdot 8H_2O$ in Moist Helium		
53 ± 2	9.4 ± 0.5	11.2	Loss of 2 H_2O
82 ± 2	21.4 ± 0.2	22.4	Loss of 4 H_2O
123 ± 4	43.3 ± 1.0	44.8	Loss of 6 H_2O + 1 HCl
	$ZrOBr_2 \cdot 8H_2O$ in Dry Helium		
43 ± 2	8.3 ± 1.0	8.7	Loss of 2 H_2O
64 ± 3	17.9 ± 0.1	17.5	Loss of 4 H_2O
122 ± 5	39.8 ± 1.0	41.5 45.9	Loss of 5 H_2O + 1 HBr Loss of 6 H_2O + 1 HBr
485 ± 20		(No assignment)	
650	61.5 ± 0.2	61.7	Dehydration to ZrO_2
	$ZrOBr_2 \cdot 8H_2O$ in Moist Helium		
53 ± 2	7.4 ± 1.0	8.75	Loss of 2 H_2O
79 ± 4	18.0 ± 0.8	17.5	Loss of 4 H_2O
147	52.0 ± 2.0	45.9 41.5	Loss of 6 H_2O + 1 HBr Loss of 5 H_2O + 1 HBr

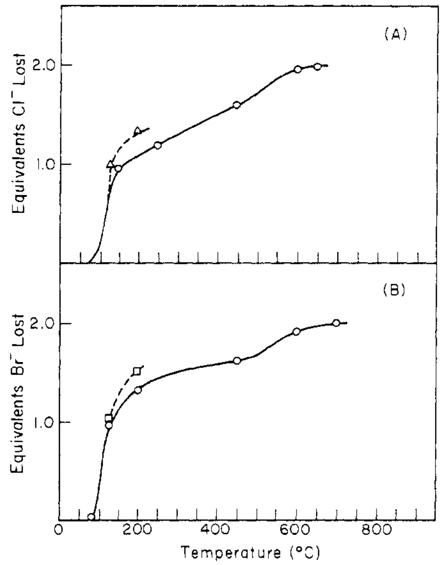

Figure 3. Loss of halide as a function of temperature for (A) $ZrOCl_2 \cdot 8H_2O$ and (B) $ZrOBr_2 \cdot 8H_2O$. Analyses done in dry helium are indicated by a solid line; those done in moist helium, by a dashed line.

uct which was halide free when tested with silver nitrate solution was obtained above 650°.

When the dehydration takes place in a stream of moist helium, considerable changes occur in the thermogravimetric traces. The steps in the dehydration, especially the first and second steps, are much better resolved. In the case of the chloride, the end point of the first step of the dehydration in dry helium appears as a barely detectable inflection in the thermogravimetric trace. In moist helium the first step is well resolved.

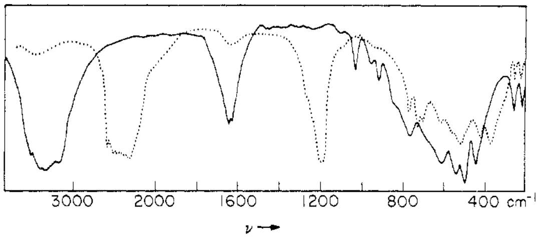

Figure 4. Infrared spectra of $ZrOCl_2 \cdot 8H_2O$ (——) and $ZrOCl_2 \cdot 8D_2O$ (····), ambient conditions.

Loss of water is retarded particularly in the first dehydration step. Two equivalents of water is not completely discharged in the first step when the dehydration takes place in a moist atmosphere. The second step corresponds closely to the cumulative loss of 4 equiv of water in both dry and moist atmospheres. The temperatures at which these steps are complete are elevated (Table I).

The loss of hydrogen halide is considerably accelerated in the dehydration in moist helium (Figure 3). This result supports a reaction scheme for the loss of halide in which no metal-halide bonds form. No evidence was found for the disproportionation reaction proposed by Takagi[3] for the loss of chloride, as in

$$2ZrOCl_2 \rightarrow ZrO_2 + ZrCl_4 \tag{1}$$

Effluent gas and the furnace walls were free of $ZrCl_4$ which sublimes at 331°. At least some water is present in these samples, even at quite high temperatures. The presence of water certainly would preclude the formation of zirconium halide bonds required for the proposed disproportionation.

The hexahydrates and the tetrahydrates have thermogravimetric traces similar to those of the octahydrates, but with the first and the first two steps missing, respectively.

The loss of the first 2 equiv of water in the first step of the dehydration of zirconium oxide halide octahydrates is readily reversed by allowing the hexahydrate to stand in a moist atmosphere. The second step of the dehydration is reversed much more slowly. A return to the octahydrate is obtained only by allowing the tetrahydrate to stand several days in a moist desiccator at room temperature. Subsequent steps could not be reversed. The products of the first two dehydration steps could be readily and completely dissolved in water. Products of later steps could not be completely dissolved and left chalky residues.

Infrared Spectra. Tentative assignments of the bands in the infrared spectra of the stoichiometric phases that appear in the dehydration of the zirconium oxide halide octahydrates are given in Table II. The spectra of the octahydrates, hexahydrates, and tetrahydrates of the chloride and bromide are very nearly the same. Resolution of structured bands, especially in the 1050-800 cm^{-1} region, improves as the hydration number decreases from 8 to 4. Most bands due to water and protonated structures are sharper and better resolved in the deuterated compounds.

We shall concentrate on the infrared spectra of $ZrOCl_2 \cdot 8H_2O$ and its deuterio analog (Figure 4), as here the interpretation is based on a known structural formulation, $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 12H_2O$. The region 3700-3000 cm^{-1} is assigned to O-H stretches. The sharp band at 3520 ± 10 cm^{-1} is attributed to the O-H stretch of bridging hydroxide. The shift of this band to 2590 ± 10 cm^{-1} upon deuteration (ν_H/ν_D = 1.36) is consistent with this assignment. Hydrogen-bonding interactions in the crystals are apparently responsible for the

Table II. Infrared Spectra of Zirconium Oxide Halide Hydrates[a]

	Freq, cm^{-1}			Freq, cm^{-1}				Freq, cm^{-1}				
Assignment	$ZrOCl_2 \cdot 8H_2O$	$ZrOCl_2 \cdot 8D_2O$	ν_H/ν_D	$ZrOCl_2 \cdot 6H_2O$	$ZrOCl_2 \cdot 4H_2O$	$ZrOCl_2 \cdot 4D_2O$	ν_H/ν_D	$ZrOBr_2 \cdot 8H_2O$	$ZrOBr_2 \cdot 6H_2O$	$ZrOBr_2 \cdot 4H_2O$	ZrO_2	
OH str	3520 s, sp	2590 s, sp	1.36		3515 s, sp	2596 s, sp	1.36	3520 s, sp		3515 s, sp		
HOH str	3470 s	2500 s	1.39		3410 s	2524 s	1.35	3460		3410 s		
	3400 s	2410 s	1.42	3300 s, b	3350 s	2475 s	1.35	3400		3340 s		
	3330 s				3220 s	2380 s	1.35	3330	3200 s, b	3210 s		
	3270 s	2330 s	1.40		3120 s	2290 s	1.36			3120		
HOH def	1640 s			1640 sh				1640 sh	1645 sh		1215 w	
		1210 s, b	1.36		1610 s	1194 s	1.35			1620 s	1100 w	overtone
	1625 s			1620 s				1610 s	1605 s		1020 w	
Bridging OH def	1028 m	775	1.33	1020 m	1020 m, sp	775 m	1.32	1005 m	1000 m	1000 m, sp		
	945 m	720	1.35	950 sh	945 m	723	1.31	940 m	940 sh	940 m		
	914 m	697	1.30	910 w	912 m	700	1.31	910 sh		910 m		
Coordinated water "rock"	835 w, b	620 b	1.35	850 w	845 w, sp	620 w	1.36	505 w, b		810 m		
$Zr-O_2-Zr$ asym str	765 m, b	(Obscured)		745 m	735 b	(Obscured)		735 b	730 b	735 m	740 s	
											610 w	
Zr-O modes	585 s	565 s	1.04	585 s	615 w	620 w	0.99	583 s	585 s	615 w		
											520 s	
	545 s	530 s	1.03	548 s	520 s	520 s	1.00	544 s	543 s	525 s		
Coordinated water "wag"	510 s	375 s	1.36	490 m	470 s	370 s	1.29	485 s	500 s, b	450 s	445, 410 d	
											373, 360 d	
Zr-O modes	445 m	425 m	1.05	450 s	(Obscured)	450		445 m	450 w			
	285 s	260 s, sp	1.09	278 s, sp	275 s, sp	270 s, sp	1.02	276 s, sp	278 s, shp	275 s, sp	278 s, sp	
	228 s	225 s, sp	1.01	240 s, sp	249 s, sp	240 s, sp	1.04	242 s, sp	243 s, shp	240 s, sp	237 s, sp	

[a] Key: sp, sharp; b, broad; sh, shoulder; d, doublet; s, strong; m, medium; w, weak.

low energy of the band relative to isolated O-H. An empirical relationship[13] between hydrogen bond length and O-H stretching frequency can be used to estimate OH· · ·Cl at 3.3 ± 0.2 Å, in good agreement with the distance of 3.42 ± 0.04 Å reported by Mak.[6] The broad, intense absorption at 3400 cm^{-1} was resolved into four bands. These bands are assigned to the symmetric and asymmetric O-H stretches of coordinated and lattice water.

In the octahydrates the HOH deformation mode gives rise to a doublet band which is particularly well resolved in the spectra of samples cooled to 93°K. As the dehydration proceeds, the high-energy member (1640 cm^{-1}) of the doublet disappears. It is a shoulder in the hexahydrate and there is only a single band (1610 cm^{-1}) in the tetrahydrate. It was not possible to resolve the doublet in spectra of deuterated species. However, the broad DOD deformation band maximum moves from 1210 cm^{-1} in the octadeuterate to 1194 cm^{-1} in the tetradeuterate. The band is much sharper in the tetradeuterate.

The band at 1028 cm^{-1} is assigned to the bridging hydroxide deformation. Deuteration moves this band to 775 cm^{-1} ($\nu_H/\nu_D = 1.32$). The band shifts to higher energy by 5-7 cm^{-1} upon cooling to 93°K. Such temperature-dependent behavior of band positions associated with bridging structures has been previously reported.[14,15]

The assignment of the bands at 945[16] and 914[16,17] cm^{-1} to the zirconyl (ZrO^{2+}) group obviously requires revision in view of the results of the crystal and molecular structure determinations.[5,6] As deuteration shifts these bands to 720 ($\nu_H/\nu_D = 1.31$) and 697 cm^{-1} ($\nu_H/\nu_D = 1.31$), respectively, a protonated structure must be involved. The band positions and shapes suggest that they be associated with the bridging hydroxides. These bands, however, lack the temperature dependence of the band at 1028 cm^{-1}. The bands show no change in position with dehydration, although they are sharpened and better resolved in the tetrahydrate than in the octahydrate. They could be associated with modes of coordinated water. At present, we are unable to make a positive assignment of these bands.

The weak, broad band at 835 cm^{-1} shifts to 620 cm^{-1} ($\nu_H/\nu_D = 1.35$) upon deuteration. Its position and shape fit well with expectations for a "rocking" mode of water coordinated to a tetrapositive ion.[18,19] The band at 510 cm^{-1} is assigned to the "wagging" mode of coordinated water. Deuteration shifts this band to 375 cm^{-1} ($\nu_H/\nu_D = 1.32$). In the spectra of the hexahydrates and tetrahydrates the "wagging" mode appears at 490 and 470 cm^{-1}, respectively.

The rest of the infrared spectrum is assigned to zirconium-oxygen motions in the tetrameric cation. The broad band at 765 cm^{-1} is assigned to an asymmetric stretch of the ZrO_2Zr bridging unit. The band persists in the spectra of all the dehydration products. The band assignment is in keeping with the predictions of a normal-coordinate analysis of MO_2M species and with bands observed in the spectra of a variety of dioxo-bridged molybdenum compounds.[20] The band is obscured by absorption due to D_2O in the spectra of the deuterated compounds. Sharp bands at 285 and 228 cm^{-1} are common to all the spectra, including that of the ultimate dehydration product, ZrO_2. They are little affected by deuteration.

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The 600-400-cm^{-1} region of the spectrum of $ZrOCl_2 \cdot 8H_2O$ is comprised of three strong bands which are assigned to zirconium-oxygen modes. This region of the spectrum is little affected as the hydration number drops from 8 to 6. However, the spectra of the tetrahydrates suggest that the zirconium ions have undergone a change in coordination number during the dehydration from the hexahydrates. Bands at 585 and 545 cm^{-1} in the octahydrates and hexahydrates collapse into a strong band at 520 cm^{-1} and a weaker band at 615 cm^{-1} in the tetrahydrates. The band at 445 cm^{-1} in the octahydrate is intensified in the tetrahydrate. Deuteration of the tetrahydrate shows the presence of absorption in this region which is not associated with a protonated structure. The positions of the seven absorption bands in the tetrahydrates in the Zr-O stretching region are strikingly similar to those in the spectrum of ZrO_2 (baddeleyite) (see Figure 5). The seven bands observed for ZrO_2 are expected in view of its distorted ZrO_7 core structure,[21] and it is probable that the tetrahydrates also contain seven-coordinate Zr(IV) central ions.

Discussion

The results of our thermal and spectroscopic studies of $ZrOCl_2 \cdot 8H_2O$ and $ZrOBr_2 \cdot 8H_2O$ support the idea that these two isomorphous species are also isostructural. Therefore, the bromide must also contain the tetrameric cation $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$. Thermal analysis indicates that the first 2 equiv of water lost in the dehydration makes little change in the structure of the compounds. These water molecules must be very loosely held in the crystal lattice. The ease with which the first step of the dehydration is reversed substantiates this proposal. The loss of the second 2 equiv of water produces a modest change in the heating rate of the material, with little effect on the crystal structure. Dramatic changes in the structure do occur, however, upon the simultaneous loss of halide and the remaining water.

The three-dimensional crystal structure[6] of $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 12H_2O$ shows that, of the three lattice water molecules per Zr(IV), two are three-coordinate and one is four-coordinate. Hydrogen bond distances are substantially the same for all three water molecules. The three-coordinate water molecules have abnormally high temperature parameters. Great uncertainty in position due to thermal motion at room temperature is the type of behavior expected for water molecules lost at less than 50°. Infrared evidence indicates that the Zr(IV) ion remains eight-coordinate after the completion of the first step of the dehydration. The first dehydration step for both halides is, therefore, assigned to the loss of the 2 equiv of three-coordinate lattice water to give $[Zr_4(OH)_8(H_2O)_{16}]X_8 \cdot 4H_2O$. The loss of the three-coordinate water molecules reduces the coordination number of the remaining lattice water equivalent to 3.

One of the four water molecules coordinated to Zr(IV) is lost in the second step of the thermal dehydrations. The four Zr-O bond lengths (2.31, 2.34, 2.21, 2.22 Å)[6] suggest that two of the coordinated water molecules are more loosely bound than the other two. One of the loosely bound water molecules doubtless is involved in hydrogen bonding to the nearby (2.69 Å) four-coordinate lattice water. We suggest that the second step of the thermal dehydration involves loss of this coordinated water molecule and the remaining lattice water, yielding $[Zr_4(OH)_8(H_2O)_{12}]X_8$. Infrared results indicate that the coordination geometry of the Zr(IV) ions in $[Zr_4(OH)_8(H_2O)_{12}]X_8$ is similar to the distorted seven-coordinate square-base, trigonal-base prism structure of ZrO_2 (baddeleyite).

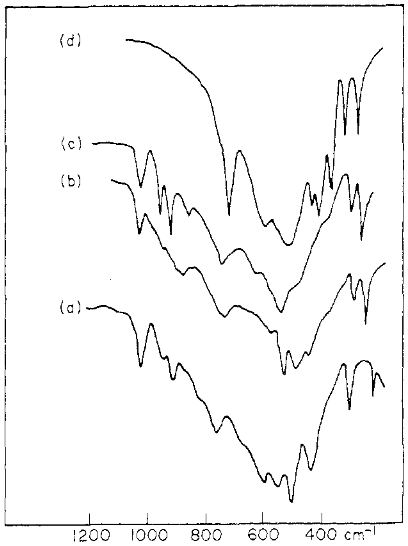

Figure 5. Infrared spectra of (a) $ZrOCl_2 \cdot 8H_2O$, (b) $ZrOCl_2 \cdot 6H_2O$, (c) $ZrOCl_2 \cdot 4H_2O$, and (d) ZrO_2, ambient conditions.

The third step of the dehydration involves the loss of 1 equiv of halide. Thermal parameters from the crystal structure of the chloride indicate that one halide ion is more loosely held than the other. It is presumably this halide ion that is lost first, but the lack of specific structural data for the bromide or either of the tetrahydrates makes it impossible to rationalize in any detail the very complex third dehydration step. Infrared evidence suggests that the dehydration products above 150° have lost most of the structural features of the parent octahydrate. They can be reasonably formulated as ZrO_2 contaminated with chloride and water.

The only band in the infrared spectrum of $ZrOCl_2 \cdot 8H_2O$ which can definitely be associated with lattice water occurs at 1640 cm^{-1}. Its position is consistent with the 1627 cm^{-1} deformation band of liquid water [22] and the 1644 cm^{-1} absorption peak observed in ice. Assignment of the high-energy component of the water deformation doublet to lattice water is further substantiated by the behavior of the bands as the sample dehydrates. However, opposite orderings have been proposed for cobalt(II) chloride hexahydrate and iron(II) chloride tetrahydrate.[23,24] Coordination would be expected to lower the frequency of the water deformation mode, whereas hydrogen bonding would raise its frequency.[25] The ordering of the deformation bands due to coordinated and lattice water depends on the relative importance of the two effects in the species of interest. Certainly in the case of $ZrOX_2 \cdot 8H_2O$ where hydrogen-bond lengths are fairly large and the central metal ion is tetrapositive, coordination should predominate.

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Registry No. $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 12H_2O$, 39388-37-9; $[Zr_4(OH)_8(H_2O)_{16}]Br_8 \cdot 12H_2O$, 39382-86-0; $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 4H_2O$, 39382-87-1; $[Zr_4(OH)_8(H_2O)_{16}]Br_8 \cdot 4H_2O$, 39382-85-9; $[Zr_4(OH)_8(H_2O)_{12}]Cl_8$, 41579-22-0; $[Zr_4(OH)_8(H_2O)_{12}]Br_8$, 41579-23-1; ZrO_2, 1314-23-4.

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