^{17}O and ^{1}H NMR study of the tetranuclear hydroxo zirconium complex in aqueous solution

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Abstract

The tetrameric hydroxo zirconium(IV) complex in aqueous solution has been studied by means of ^{17}O and ^{1}H NMR. For the first time, an ^{17}O NMR signal from oxygens coordinated to Zr in this complex has been observed. This signal, at ~ 180 ppm, corresponds to ~ 2 O/Zr and has been assigned to two strongly bound terminal water molecules. Exchange of these waters with the bulk water takes a few months, as found by addition of ^{17}O-enriched water. In ^{1}H NMR spectra, besides the bulk water signal, a signal at 7.9 ppm has been observed at room temperature and assigned to slowly exchanging protons, 2H/Zr, of the terminal water molecules in the tetramer. The lifetime of a specific proton of this type is unusually long for inorganic coordination compounds in aqueous solution, ≈ 0.1 s in 2.2 M Zr solution at room temperature. On this basis, the formula of the tetramer in aqueous solution should be written $[Zr_4(OH)_8(H_2O)_8^{I}(H_2O)_8^{II}]^{8+}$, i.e. there are two inert and two labile water molecules per Zr. Up to two of the coordinated water protons are so easily dissociated that this species constitutes a very strong acid. One of the inert water molecules is replaced completely upon addition of one nitrate per Zr. Addition of acetone to an aqueous solution of the tetramer leads to coordination of acetone to the tetramer.

Introduction

Zr(IV) is known to be hydrolyzed even in very acidic aqueous solutions. The large amount of experimental results from solution chemistry studies of this metal ion has been reviewed, for example, by Solovkin and Tsvetkova [1], Larsen [2] and Baes and Mesmer [3]. The predominant hydrolyzed species are polynuclear even in very dilute ($>10^{-4}$–10^{-3} M) solutions of high acidity (1–2 M). A variety of experimental techniques (spectrophotometry [4], ultracentrifugation [5], light scattering [6] etc.) have been used to characterize these species. Complexes such as $Zr_3(OH)_4{}^{4+}$ and $Zr_4(OH)_8{}^{8+}$ have been suggested. In some investigations formation constants have been derived from the experimental data, although the systems are known to attain equilibrium very slowly.

Direct evidence for the existence of tetranuclear complexes comes from the determination of the crystal structure of $ZrOCl_2 \cdot 8H_2O$ [7, 8]. This compound contains the $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ cation (Fig. 1) in which four Zr atoms at the corners of a slightly puckered square are connected by double hydroxo bridges. Four water molecules are also attached to Zr, giving a coordination polyhedron of a distorted dodecahedron. Large angle X-ray scattering measurements [9, 10] of concentrated aqueous solutions of zirconium(IV) and hafnium(IV) halides and zirconium(IV) perchlorate are consistent with a predominant tetranuclear species with a structure similar to that of the cation in the solid. Further structural support comes from an EXAFS study, where results from zirconium nitrate solutions are compared with those from crystalline $ZrOCl_2 \cdot 8H_2O$ [11].

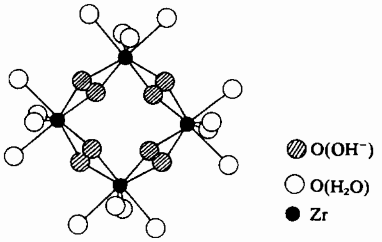

Fig. 1. The structure of the $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ cation in the crystals of $ZrOCl_2 \cdot 8H_2O$ [8].

^{1}H NMR spectra of zirconium perchlorate in water–acetone mixtures at −70 °C show two separate signals, each corresponding to four hydrogen atoms per zirconium. The authors [12] assumed that these signals are due to protons in bound water molecules which would be in accordance with the complex composition $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$. The lack of a separate NMR signal for the hydroxo protons can be caused by rapid exchange. On the other hand, ^{1}H NMR spectra of aqueous solutions of zirconium perchlorate or chloride

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at 10 °C show only one signal to high frequency from the bulk water signal [13]. This signal corresponds to 2 water protons for each Zr atom in the perchlorate solution and to 1.5 in the chloride solution. In analogy with aluminium the hydroxo protons are assumed to exchange rapidly with the bulk water protons [14]. The number of protons/Zr decreases on the addition of NaOH. At temperatures below 0 °C two new small signals to high frequency from the bigger one are obtained. These observations are explained by assuming a further polymerization. In a later investigation where ^1H NMR has been used for solutions of $ZrOCl_2$ in $HClO_4$ a signal corresponding to two slowly exchanging protons/Zr atom has, however, been assigned to hydroxo protons [15].

Raman spectra of concentrated acidic aqueous solutions of zirconium chloride show a polarized band at 580 cm^{-1} and a depolarized band at 450 cm^{-1}, assigned to Zr–OH vibrations of the tetrameric cation, and a shoulder at $\sim$420 cm^{-1}, assigned to a $Zr–OH_2$ vibration [16]. On the addition of NaOH the shoulder decreases and a new band appears at $\sim$530 cm^{-1} which is explained as due to Zr–OH vibrations involving terminal hydroxo groups, e.g., $[Zr_4(OH)_8(OH)_4(H_2O)_{12}]^{4+}$. In a more extensive and quantitative study Raman spectroscopy has recently been used in combination with ^1H NMR on aqueous solutions of zirconium(IV) chloride at varying concentrations and degrees of hydrolysis [17–19]. The data are explained by assuming the tetramer $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ as the major complex in aqueous solutions. On the addition of OH^- ions the double hydroxo bridges are replaced by single oxo bridges, a conclusion drawn from the weak isotopic shifts observed for some Raman bands after deuteration. A predominant polynuclear species containing eight Zr atoms is suggested. The ^1H NMR spectra recorded at 0 °C at different degrees of hydrolysis show a separate signal corresponding to at most 1.57 H/Zr, which decreases as the concentration of Zr is decreased or that of OH^- is increased. This signal is assigned to protons in the bridging OH^- groups.

Other methods have also been used to study the hydrolysis and structure of the tetrameric Zr(IV) cation. Solutions of $ZrOCl_2$ have been investigated by electron microscopy after refluxing up to 24 h until a precipitate is formed [20]. The results indicate that polymerization takes place by formation of double hydroxo bridges between tetramers as a first step in a way originally suggested by Clearfield [21]. This conclusion is also supported by the EXAFS study, where the number of the bridged and the diagonal Zr–Zr distances increase when the OH/Zr ratio is increased above $ZrO(NO_3)_2$ [11]. The final product is monoclinic zirconium dioxide (baddeleyite) with a distorted fluorite structure in which the coordination number of zirconium is seven [22, 23]. Results from thermal dehydration and IR spectroscopic studies of solid $ZrOCl_2 \cdot 8H_2O$ are explained by suggesting that one of the four coordinated water molecules per zirconium is lost at the same temperature as the last, more tightly bonded, lattice water molecules leave the tetranuclear complex. In the resulting species, $[Zr_4(OH)_8(H_2O)_{12}]^{8+}$, the coordination number of Zr has decreased from eight to seven [24]. This is supported by the observation that one of the complex waters is strongly hydrogen-bonded to lattice water in the crystal state and also more loosely bonded to Zr [8]. The final dehydration product is monoclinic ZrO_2. There is also further support for the assumption that one H_2O/Zr is different from the others and can rather easily be deprotonated forming terminal hydroxo groups [25]. In a later investigation, more complicated polymeric species with both hydroxo and oxo bridges are suggested to be formed at temperatures above 80 °C [26].

Recently, results from ^{17}O NMR measurements on 2 M solutions of $ZrOCl_2$ in aqueous HNO_3 have been published. Only signals from bulk water and nitrate have been observed, e.g. no signal from coordinated oxygens [27].

It is thus obvious that protons with quite different exchange rates are present in the tetranuclear Zr(IV) complex. But, despite the numerous experimental studies [4–27] the interpretation of the experimental facts is still a matter of controversy. How many protons of each kind are present in the complex? Which of them belong to coordinated water and which to hydroxo groups? The aim of the present study has been to analyze the combined results from ^1H and ^{17}O NMR using a high field NMR spectrometer with the intention of receiving more unambiguous structural and kinetic information on the system.

Experimental

Materials, preparation and analysis

A stock solution of zirconium perchlorate was prepared by dissolving $ZrO(ClO_4)_2 \cdot 8H_2O$ (Johnson Matthey, reagent grade) in water without further purification. The amount of perchlorate was determined by passing a portion of the solution, from which the zirconium ions had been removed by precipitation and filtration as hydrous oxide, through an H^+-saturated cation exchanger (DOWEX 50W-X8). The free acid was then titrated with standardized NaOH. The investigated solutions were prepared from the stock solution (1.363 mol Zr per kg solution) and the appropriate diluent by weighing. Concentrated HNO_3, acetone (Merck, Darmstadt, Germany), acetone-d_6 (Ciba-Geigy, Basel, Switzerland; 99.5% or 99.95%) and ^{17}O-enriched water (ISO-YEDA Co., Rehovot, Israel; 12.3% or

17.55% ^{17}O), all of reagent grade, were used as received. The densities of the solutions were determined with an Anton Paar digital densitometer, DMA35.

The investigations were started using aqueous zirconium chloride solutions. A precipitate was formed when these solutions were mixed with acetone and, therefore, perchlorate was finally chosen instead of chloride.

NMR measurements

^1H NMR spectra were recorded at 400.1 MHz on a Bruker AM400 spectrometer using 5 mm (outer diameter) spinning sample tubes. Different probe temperatures were achieved using a Bruker VT1000 variable temperature control unit. The temperature was measured by a calibrated Pt-100 resistance thermometer. Spectra for aqueous solutions were recorded in unlocked mode, whereas for acetone–water solutions internal acetone-d_6 was used as the field lock. The NMR parameters were chosen to obtain quantitative integrated intensities for the measured signals (pulse width $= 4$ $\mu s \approx 15$–$20°$, pulse repetition time $\geqslant 0.4$ s). The spectra were recorded within 12 h after mixing the aqueous solutions with acetone-d_6. The chemical shifts are given in ppm toward higher frequency with respect to internal or external acetone at 2.04 ppm, which corresponds to TMS at 0 ppm.

^{17}O NMR spectra were recorded at 54.2 MHz using 10 mm (outer diameter) spinning sample tubes. The spectrometer, temperature control unit and temperature measuring device were the same as for the ^1H NMR measurements. Some typical NMR parameters: pulse width $= 15$ μs ($\sim 80°$ pulse), number of scans $> 25\,000$, spectrum width $= 62.5$ or 125 kHz, pulse repetition time $= 130$ ms. The spectra for the solutions in water/acetone solvent were recorded within 12 h after mixing the aqueous solutions with acetone. The chemical shifts are given in ppm toward higher frequency with respect to external tap water at 25 °C.

In order to correct for the non-uniform power distribution along the spectrum and hence to obtain quantitative ^{17}O NMR spectra, calibration curves for different settings of the transmitter frequency were recorded for the two widths of the spectral window. A solution containing water and acetone in equal amounts was measured. The intensity reduction was $\leqslant 15\%$ even for the signals recorded in the outermost parts of the spectral window.

^{91}Zr NMR spectra were recorded at 37.2 MHz for a 0.5 M aqueous $(NH_4)_2ZrF_6$ solution. As expected [28], one signal was obtained. The half-width was 1180 Hz at 25 °C and 545 Hz at 70 °C. However, a solution containing the tetrameric zirconium species gave no signal, probably because of the fast quadrupolar relaxation of the ^{91}Zr nucleus.

Raman measurements

Raman spectra were recorded on a DILOR Z24 triple monochromator, equipped with a single channel, photon counting detector. Both the 647.1 and 514.5 nm lines of Coherent Innova 90K krypton ion and 90-5 argon ion lasers, respectively, were used to excite the Raman spectra. Plasma lines were removed with an Applied Photophysics 2300 laser filter monochromator. Spectral band widths of 4 cm^{-1} were used.

Polarization measurements were made using a polarization analyzer plate followed by a quarter-wave quartz scrambler in the light path after the sample. The wavenumber scale was calibrated using CCl_4 [29] and the frequencies given are accurate within ± 2 cm^{-1}.

Results

Raman spectra

The Raman spectrum of a concentrated (2.2 M) aqueous solution of $ZrOCl_2$ shows bands at 581(s, polarized), 454(s), 420(sh), 284(w) and 156(m) cm^{-1}. Bands with the same frequencies (and ClO_4 frequencies) were observed for a 2.0 M aqueous solution of $ZrO(ClO_4)_2$. In the Raman spectrum of solid $ZrOCl_2$ bands with similar frequencies (588(s), 459(s), 424(sh), 295(w), 262(w), 192(m), 157(m), 118(s), 86(m), 62(w) and 44(m) cm^{-1}) to those in the solution are present.

^{17}O NMR data

Aqueous solutions

Two portions of the stock solution were placed in NMR tubes (O1 and O2). To one of the portions (O2) 0.5 ml of 12.3% ^{17}O-enriched water was added. The solutions were kept at +55 °C. After 6, 10 and 17 days ^{17}O NMR spectra were recorded at varying temperatures. The spectra for the solutions O1 and O2 are essentially similar: besides the peaks of bulk water (~ 10 ppm) and the perchlorate ion (~ 290 ppm), a broad peak at ~ 180 ppm appears. The area of this peak in the natural abundance solution (O1) corresponds to approximately 2 O/Zr. Adding ^{17}O-enriched water to the solution O1 leads to slow enrichment of this peak; its area increases slowly up to 2 O/Zr after a few months. The same result is obtained if acetone is added to the solution before the NMR measurement.

Also, three additional, narrow and small peaks show up at ~ 230, 278 and 281 ppm. Their area increases slightly with prolonged heating time and is at most a few percent of the broad peak. The spectra for solutions O1 and O2 are shown in Fig. 2.

The spectrum of a solution containing only ~ 2 M HNO_3 (i.e. no Zr) shows, besides the bulk water signal, a singlet of nitrate at 416 ppm. When concentrated

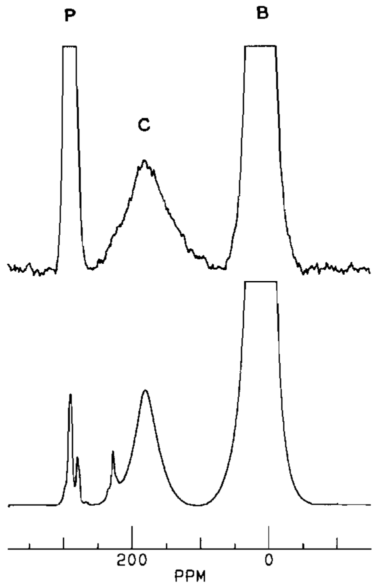


Fig. 2. ^{17}O NMR spectra of concentrated zirconium(IV) perchlorate solutions in water recorded at 54.2 MHz. The signals arising from perchlorate (P), coordinated (C), and bulk water oxygens (B) are labelled. (a) Natural isotopic abundance, [Zr] = 2.2 M, (Zr/H_2O = 1:25), T = 45 °C (solution O1). (b) Solution enriched in ^{17}O (~ 1.8%), [Zr] = 2.0 M, (Zr/H_2O = 1:29), T = 65 °C (solution O2).

HNO_3 was added to solution O1, so that $[NO_3]_{tot} \approx 2$ M, (solution O7, see Table 1) the area of the 180 ppm peak decreased to ~ 0.6 O/Zr. When the same amount of HNO_3 was added to the ^{17}O-enriched solution (solution O8; prepared from solution O2 equilibrated 10 months after addition of $H_2{}^{17}O$, see Table 1), this area became ~ 1.0 O/Zr. The peak at 230 ppm was not present in the latter solution, but two new, small and narrow peaks appeared at 396 and 415 ppm (ratio ~ 1:3), respectively. (The latter was probably caused by a minor amount of non-coordinated nitrate, partially enriched in ^{17}O.)

Solution in water/acetone solvent

Portions of the stock solution were mixed with ^{17}O-enriched water and were kept for various periods and at different temperatures (Table 1). A few hours before NMR measurements acetone was added to slow down the chemical exchange and to lower the viscosity of the solution without decreasing the ratio Zr/H_2O too much. ^{17}O NMR spectra were measured at temperatures between −5 and +45 °C. Without ^{17}O-enrichment (solution O3) only three signals were observed: acetone, perchlorate and bulk water. After a short time of enrichment (solution O4) two additional signals appeared: a large, broad one at ~ 180 ppm and a narrow, small one at ~ 230 ppm. The peaks become narrower at higher temperature and correspond in total to about 0.5 O/Zr. After longer enrichment times the two signals (measured at +45.6 °C) increase up to about 0.8 (solution O5) and finally to 1.9 O/Zr (solution O6).

(Interestingly, acetone is exchanging oxygen with bulk water and accordingly, after a few hours the ^{17}O content is completely equilibrated between the two solvents. Detailed investigation of this reaction is outside the scope of the present work.)

Solutions in water/acetonitrile solvent

Acetonitrile was also tried as a solvent in order to get narrower signals/better resolution by increasing the measuring temperature above the boiling point of acetone. Only peaks of bulk water and perchlorate were observed; in addition, a broad feature centered at about 160–170 ppm appeared at the highest temperature used (+80 °C). The latter feature was too broad to be integrated.

^1H NMR data

Aqueous solutions

Portions of the stock solution were diluted with water. ^1H NMR spectra were measured at temperatures between −3 and +38 °C. Two signals were obtained; a

TABLE 1. Data on the Zr(IV) perchlorate solutions investigated by ^{17}O NMR

Solution	Enrichment % $^{17}O^a$	Equilibration time	Mole ratio $Zr:H_2O:acetone:HNO_3{}^b$	Mole ratio O/Zr^c
O1			1:24.7:0:0	2.0
O2	1.8	6–17 days (55 °C)	1:29.0:0:0	~ 1[d]
O3			1:24.7:89.3:0	not obs.
O4	0.4	4 days (4 °C)	1:27.4:86.1:0	0.5
O5	0.9	2 weeks (45 °C)	1:30.6:84.8:0	0.8
O6	1.0	4 months (60 °C)	1:31.0:84.0:0	1.9
O7		2 days (25 °C)[e]	1:25.8:0:1.1	0.6
O8	1.5	2 days (25 °C)[f]	1:30.2:0:1.1	1.0

[a] Analytical value. Observe that perchlorate oxygens are not enriched. [b] Analytical composition. [c] Obtained from ^{17}O NMR peak integrals. [d] After 17 days of equilibration. [e] Solution O1, add HNO_3, 2 days of equilibration (at 25 °C). [f] Solution O2 (10 months of equilibration after addition of ^{17}O), add HNO_3, 2 days of equilibration (at 25 °C).

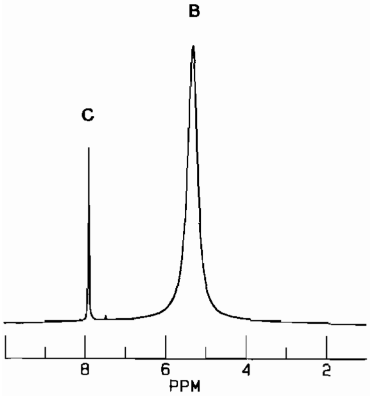


Fig. 3. ^1H NMR spectrum of 2.2 M zirconium(IV) perchlorate solution (H1) recorded at 400 MHz, $T = -3.1$ °C. The signals arising from hydrogens bonded to coordinated oxygens (C) and bulk water hydrogens (B) are labelled.

TABLE 2. Compositions of and results from ^1H NMR measurements on aqueous Zr(IV) perchlorate solutions (no acetone added; coordinated proton signal is indexed by C, bulk proton signal by B)

Temperature (°C)	δ^C (ppm)	$\Delta\nu^C_{1/2}$ (Hz)	δ^B (ppm)	$\Delta\nu^B_{1/2}$ (Hz)	$\nu^C-\nu^B$ (Hz)	Mole ratio H/Zr[a]
Solution H1 (Zr:H_2O = 1:24.7, [Zr] = 2.174 M, [H_2O] = 51.6 M)						
−7.1			1.05			
−3.1	3.22	7	0.65	110	1029	2.3
+11.3	3.19	10	0.65	45	1018	1.9
+24.2	3.08	42	0.47	25	1042	2.1
+30.9	3.11	73	0.55	28	1027	1.7
+38.2		300	0.54	34		
Solution H2 (Zr:H_2O = 1:50.6, [Zr] = 1.082 M, [H_2O] = 53.6 M)						
−3.1	3.43	6	0.49	47	1175	1.9
+11.3	3.39	13	0.42	28	1188	1.0
+24.2	3.30	95	0.25	21	1222	1.3
+30.9	3.28	173	0.27	24	1207	
+38.2				26		
Solution H3 (Zr:H_2O = 1:102, [Zr] = 0.539 M, [H_2O] = 54.5 M)						
+11.5	3.32	36	0.16	18	1263	0.9
+24.6	3.34	150	0.13	25	1284	
Solution H4 (Zr:H_2O = 1:208, [Zr] = 0.266 M, [H_2O] = 55.0 M)						
+11.5	3.34	44	0.12	13	1289	0.4
+24.6			0.03	18		

[a]Obtained from ^1H NMR peak integrals.

typical spectrum is shown in Fig. 3. Some results are given in Table 2. For solutions H3 and H4 only the middle part of the temperature interval could be used: the lowest temperature was below the freezing point of the solutions and at the higher temperatures the small peak was so much broadened that it could not be observed.

When HNO_3 was added (0.5 ml concentrated HNO_3 into 3 ml of solution H1, so that $[NO_3]_{tot} \approx 2$ M), in the ^1H NMR spectrum the coordinated proton peak area (linewidth = 55 Hz) corresponded to only ~1.0 H/Zr. It was located +2.0 ppm from the bulk water peak (linewidth = 40 Hz).

For a 2.0 M zirconium chloride solution with 1.1 OH/Zr analytical excess above the mole ratio corresponding to the tetramer, the area of the small ^1H signal decreased to 0.3 H/Zr.

Water–acetone mixtures

Preliminary measurements have shown that solutions prepared from acetone and acetone-d_6 give similar ^1H NMR spectra, that acetone-d_6 does not contain any impurities with signals in the region of interest, and that the signal of acetone-d_6 has a chemical shift which is neither dependent on the temperature nor on the composition of the solution.

Portions of the stock solution were mixed with acetone-d_6 the same day as the measurements were performed. Two series of spectra were recorded, one with varying temperature and the other with varying mole ratio Zr/acetone-d_6. A typical spectrum is shown in Fig. 4. Three bands are observed for all solutions, two singlets corresponding to hydrogens in acetone-d_6 and in the bulk water, respectively, and a very complex band centered approximately at 8 ppm. Selective $^1H\{^1H\}$ decoupling experiments were performed on the complex band but no individual signals within this band were found to be spin–spin coupled to other protons. In addition, the ^1H–^1H COSY spectrum supported this conclusion.

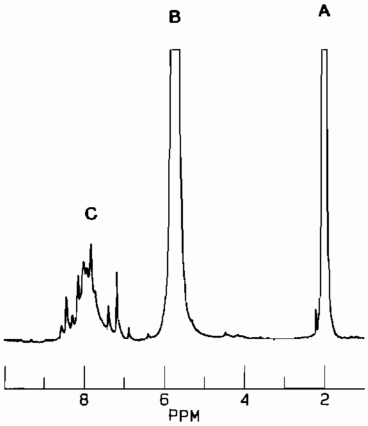


Fig. 4. ^1H NMR spectrum of a zirconium(IV) perchlorate solution in water–acetone-d_6 mixture (solution O3) recorded at 400 MHz, $T \approx -30$ °C. The signals (bands) due to hydrogens bonded to coordinated oxygens (C), bulk water hydrogens (B) and acetone-d_6 hydrogens (A) are labelled.

Discussion

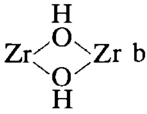
Raman spectra

Our Raman spectra of concentrated aqueous solutions of zirconium(IV) are in agreement with the spectra obtained previously by Burkov *et al.* [16] and Hannanc and co-workers [17–19]. The solution spectra are similar to the spectra recorded for solid $ZrOCl_2$ (see 'Results'); the latter is known to contain the tetramer in the crystal structure [8]. Therefore, we conclude that our aqueous solutions studied by NMR contain predominantly the zirconium(IV) tetramer.

^{17}O NMR

We assign the peak at 180 ppm to oxygens coordinated to Zr in the tetrameric species. This assignment is based on the exceptional stability of the tetramer: practically all zirconium in aqueous solution is present in this form as judged from the Raman results (*vide supra*) and from the general agreement in the literature [9–27, 30].

Moreover, we propose that the peak at 180 ppm originates from terminal oxygens, rather than from the OH bridges (see Fig. 1). This proposal is supported by the stability of the tetramer, which makes an opening of the tetramer ring less probable. In concentrated solution, the tetramer is not altered by addition of 0.3 M $HClO_4$ even after long heating at +95 °C. The



$\mathrm{Zr}\genfrac{}{}{0pt}{}{\overset{\mathrm{H}}{\mathrm{O}}}{\underset{\mathrm{H}}{\mathrm{O}}}\mathrm{Zr}$ bridges resist also large excess of hydroxide and long heating [10]. Similar stability of a double hydroxo bridge has been found for Rh(III) in the dimeric species $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(OH_2)_4]^{4+}$ [31]. In the latter case, three ^{17}O NMR signals were observed in natural abundance aqueous solutions: one for the bridging OH groups and two for the terminal water molecules (*cis* and *trans* to the OH bridge). When $H_2{}^{17}O$ was added only the coordinated water molecules were enriched in ^{17}O. The OH-bridging oxygens were not enriched at all even after one year of equilibration [31].

Moreover, addition of HNO_3 into a solution of the tetramer, so that $NO_3/Zr = 1$, decreases the area of the 180 ppm peak from 2.0 to 1.0 O/Zr. This is probably caused by complex formation between the tetramer and the nitrate ions. Such complex formation has previously been observed by Fratiello *et al.* [12]. The nitrate ions replace the coordinated water molecules so that when one NO_3^- enters the complex, one of the inert water molecules leaves it. This could be interpreted as monodentate coordination of the nitrate ion to Zr; however, it is possible that the coordination of a nitrate ligand is bidentate, releasing one strongly bound water molecule (slowly exchanging and hence observed in the ^{17}O NMR spectra) and one loosely bound water (exchanging too fast and hence unobserved in the spectra).

The other oxygen-containing species in the solution, ClO_4^-, was not expected to be enriched because of the long oxygen lifetime in this oxyanion.

In the crystal structure of $ZrOCl_2$ [8], containing the species $Zr_4(OH)_8(H_2O)_{16}{}^{8+}$ (see Fig. 1), two of the four coordinated water molecules per Zr are more tightly bound to Zr, as can be judged from the significantly different Zr–O bond lengths: 2.21, 2.22, 2.31 and 2.34 Å. Therefore, it is possible that in solution these two water molecules exchange slowly enough with the bulk water, so that this exchange is governed by slow exchange regime on the actual ^{17}O NMR time scale and hence can be observed in the spectra.

We have neither observed ^{17}O NMR signals from the OH bridges nor from the other two Zr-coordinated water oxygens. This may be caused by (i) fast quadrupolar relaxation, (ii) a small peak hidden under the large bulk water peak or (iii) fast chemical exchange on the actual NMR time scale between the coordinated and the bulk water.

The peak at 230 ppm is small but grows at prolonged heating up to ~5% of the broad peak area. It can be assigned to a slowly exchanging decomposition product of the tetramer. This product may be identical with the β-hydroxide, previously suggested by Zaitsev on chemical grounds [32].

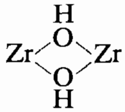
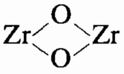
^{17}O NMR spectra have previously been recorded for aqueous solutions containing the tetrameric species, but no signal due to Zr-coordinated oxygens has been observed [27]. The reason for this failure was probably that the investigated solutions contained nitrate ions. The nitrate coordinates to the zirconium in the tetramer and replaces the coordinated water molecules (*vide supra*). In fact, coordinated nitrate ions have been observed by ^{17}O NMR as a broadening (due to quadrupolar relaxation?) and a slight shift of the nitrate signal [27].

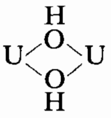
^{17}O chemical shifts for hydroxo compounds in water have previously been determined for Ir(III) [33], Rh(III) [31] and Mo(III) [34]. For Ir and Rh, the terminal water signals have been found at about −120 to −150 ppm, and for Mo at −40 ppm. For the OH oxygens, the chemical shift is −300 to −320 ppm for Rh and +124 ppm for Mo. These values do not fall in the same chemical shift region as that observed for Zr(IV) but the large differences between the corresponding shifts for Rh(III)/Ir(III) and Mo(III) show that the positions of ^{17}O NMR peaks is not always predictable.

^{1}H NMR. Aqueous solutions

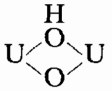
We assign the slowly exchanging proton peak to the terminal water molecules bound to Zr in the tetramer.

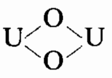
Similar ^1H NMR peaks up-frequency from the bulk water resonance have previously been found and assigned in the same way, e.g. for aqueous solutions containing $Be(OH_2)_4^{2+}$, $[Be(OH_2)_3]_2(OH)^{3+}$ and $[(H_2O)_2BeOH]_3^{3+}$ [35], and for rhodium(III) monomer $Rh(OH_2)_6^{3+}$, dimer $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(OH_2)_4]^{4+}$ and trimer $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(OH_2)_2(\mu\text{-}OH)_2Rh(OH_2)_4]^{5+}$ [31].

From the peak integrals, the concentration of the slowly exchanging protons is about 2 H/Zr in the 2.2 M Zr solution and decreases to 0.4 H/Zr upon dilution to 0.27 M. This ratio also decreases, down to 0.3 H/Zr, when the concentration of the OH^- ion is increased to 1.1 M above $ZrO(ClO_4)_2$ in the 2.2 M Zr solution. It has been suggested [18] that this is caused by a structural change so that the  $\mathrm{Zr}\genfrac{}{}{0pt}{}{\overset{\mathrm{H}}{\mathrm{O}}}{\underset{\mathrm{H}}{\mathrm{O}}}\mathrm{Zr}$ bridges become Zr–O–Zr or  $\mathrm{Zr}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}\mathrm{Zr}$ bridges. However, such a structural change would alter the Zr–Zr distances. For example, the Zr–Zr distance in compounds containing double hydroxo bridges is about 3.57 Å, whereas the corresponding distance in compounds with Zr–O–Zr bridges is ~3.89 Å [36]. Similar changes of the metal–metal distance have been observed in the crystal structures of uranyl(2+) compounds:

for  $\mathrm{U}\genfrac{}{}{0pt}{}{\overset{\mathrm{H}}{\mathrm{O}}}{\underset{\mathrm{H}}{\mathrm{O}}}\mathrm{U}$

bridges the U–U distance is 3.94 Å,

for  $\mathrm{U}\genfrac{}{}{0pt}{}{\overset{\mathrm{H}}{\mathrm{O}}}{\mathrm{O}}\mathrm{U}$ 3.78 Å

and for  $\mathrm{U}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}\mathrm{U}$ 3.69 Å [37].

A change in the metal–metal distance of this order of magnitude is normally easy to observe by large-angle X-ray diffraction techniques. However, such a change has not been observed in the radial distribution curves obtained from X-ray diffraction studies on aqueous solutions containing the zirconium tetramer [10]. In this light, the structural alteration (formation of oxo bridges) proposed by Hannane *et al.* [18] seems less probable.

This argument also confirms our assignment of the peak at 7.9 ppm to terminal water molecules, rather than to the OH protons, since the dissociation of the latter would lead to oxo bridges and hence would change the Zr–Zr distance.

We propose an alternative explanation for the variation of the number of the slowly exchanging protons with the composition of the solution. In the concentrated solution, where the formal ionic strength is about $I = 20$ M, the perchlorate ions attach to the tetramer and form an outer sphere complex, thus hindering the exchange between the coordinated and bulk water protons. Upon dilution the relative concentration of the outer sphere complex decreases, that of water increases and the proton exchange becomes fast on the actual NMR time scale. This is a kinetic effect. Also, there might be a thermodynamic effect, namely that the degree of proton dissociation is relatively limited in very concentrated solutions and increases upon dilution.

Our explanation is in accordance with the fact that the terminal water protons in hydroxo bridged species of metal ions are much more acidic than the bridging OH protons [38].

It is interesting to note that when $ZrOCl_2$ is dissolved in water the solution is very acidic, even more so than for the same concentration of HCl. The pH of a 0.055 M Zr solution is ~1.15 after the equilibrium is reached (~1 day) [20]. This corresponds to about 1.3 dissociated protons/Zr, i.e. 0.7 of the 2 slowly exchanging protons/Zr are still undissociated. This is in qualitative agreement with our ^1H NMR results for the most dilute solution (H4, see Table 2) considering that (i) the variation of the ionic strength and hence of the activity coefficients in the concentrated solutions influences the pH measurement and (ii) the accuracy of the NMR integrals is lowered in the presence of the dominating bulk water signal.

When HNO_3 is added to a concentrated solution of the tetramer, the number of the slowly exchanging protons decreases from 2 to 1. This change can be caused by the replacement of the slowly exchanging coordinated water molecules by the nitrate ions.

Kinetics

As can be seen in Table 2, the linewidth of the coordinated proton signal (due to the slowly exchanging protons in the tetramer) varies with temperature as well as with the concentration of the solution. This variation is due to proton exchange between the tetramer and the bulk water. The data have not been interpreted in terms of rate law and reaction mechanisms, since in these solutions the activity coefficients are certainly not even approximately constant. Still, it is noteworthy that the lifetime of a specific proton of the above mentioned type decreases with decreasing Zr concentration: from ~0.1 s in the 2.2 M solution to ~0.01 s in the 0.54 M solution at room temperature. This may be due to increased water activity if the rate equation for this exchange reaction is of the type: rate $=k[\mathrm{Zr}][\mathrm{H_2O}]$.

From the long lifetime of the protons we can draw the conclusion that they must belong to the slowly exchanging water molecules. The latter have a lifetime $\tau > 10^{-4}$ s, as can be judged from the chemical shift difference in the ^{17}O NMR spectra (Fig. 2), whereas the remaining coordinated water molecules, not observed by ^{17}O NMR, have $\tau < 10^{-4}$ s and hence are not compatible with the long proton lifetime. However, this conclusion is valid only under the assumption that fast chemical exchange between the unobserved water molecules and the bulk water is the reason for the absence of the corresponding coordinated water signal in the ^{17}O NMR spectra (see 'Discussion', ^{17}O NMR above).

^{1}H NMR. Water–acetone mixtures

Our results show that in solutions containing the tetramer, water and acetone the latter competes with water and coordinates to the tetramer if the acetone/water ratio is high enough. For example, already in a solution containing Zr:H_2O:acetone = 1:25:20 acetone coordinates to the tetramer. This coordination increases with increased acetone/water ratio. The number of acetone-protons coordinated in this way can be obtained from the ^{1}H NMR peak integrals and was found to vary a lot depending on the composition of the solution. In a typical solution, Zr:H_2O:acetone = 1:25:85, the mole ratio of H/Zr is ~6 and does not change significantly when the temperature is varied between −90 and −30 °C. At higher temperatures the NMR peak (C in Fig. 4) broadens and finally escapes detection because of fast chemical exchange with the bulk.

Recently, we have found that acetone coordinates to hydrolyzed rhodium(III) complexes in water/acetone solution [31]. Also nitrate coordinates to the Zr tetramer (see above [27]).

No signals due to coordinated acetone have been observed in the ^{17}O NMR spectra. However, this can be explained by rapid quadrupolar relaxation and/or by fast exchange regime on the actual ^{17}O NMR time scale.

In ^{1}H NMR spectra for related Al(III) and Rh(III) complexes, signals assigned to doubly-bridging OH groups have been observed at 4.8 [39], ~3.6 (dimer) and 4.3 (trimer) ppm [31], respectively. We have tried to find a corresponding signal in solutions of the zirconium tetramer by varying the composition of the solutions and the temperature at which NMR spectra were recorded. Unfortunately, in the present case no such signal has been observed largely because of the strong acetone affinity for zirconium. As a result, at higher acetone/water ratio acetone coordination to the tetramer gives rise to a number of overlapping signals in the region of interest (band C, Fig. 4). When the ratio is decreased, lowering the temperature leads to freezing of the solution before the slow exchange limit on the actual NMR time scale is reached.

Fratiello *et al.* [12] have measured ^{1}H NMR spectra for water/acetone solutions containing the tetramer and observed two broad signals which they assigned to 2+2 coordinated water molecules per Zr in $\mathrm{Zr_4(OH)_8(H_2O)_{16}}^{8+}$. In the light of our results this assignment is probably erroneous since in their solution the Zr:H_2O:acetone ratio was 1:10:100. In such solutions, considerable coordination of acetone molecules to the tetramer can be expected.

Conclusions

Despite the continuing interest in the polynuclear hydroxo complexes of Zr(IV) [4–27], it has been very difficult to obtain new and unambiguous information on this chemical system in solution. The present NMR study resulted in a new formulation of the composition of the tetranuclear zirconium complex in aqueous solution, $[\mathrm{Zr_4(OH)_8(H_2O)_8^{I}(H_2O)_8^{II}}]^{8+}$. This was possible through the first ^{17}O NMR observation of the oxygens coordinated to zirconium in this complex. This signal has been assigned to two slowly exchanging terminal water molecules per Zr in the complex. The exchange rate of these water oxygens is very slow; a few months is needed for complete exchange. This can be compared to $\mathrm{Ru(H_2O)_6}^{3+}$ and $\mathrm{Rh(H_2O)_6}^{3+}$, where the lifetime of a water molecule is $\tau \approx 3\times10^5$ s ($\approx$3.5 days) and 5×10^8 s ($\approx$16 years), respectively [40].

Also, two slowly exchanging protons per Zr were observed by means of ^{1}H NMR and assigned to the terminal water molecules in the tetramer. The (thermodynamically) easy dissociation of these protons makes the tetramer a strong acid and can be seen as a further step of Zr(IV) hydrolysis leading finally to polymerization of two tetramers to an octamer etc., through double hydroxo bridges.

The long lifetime of such a proton, $\tau \approx 0.1$ s at room temperature, is unusual for inorganic coordination compounds in aqueous solution. It can be compared to $\tau = 10^{-4}$ s in $\mathrm{Be(H_2O)_4}^{2+}$ [41], $\tau \approx 10^{-4}$ s in $\mathrm{Al(H_2O)_6}^{3+}$ [42, 43], $\tau \approx 2\times10^{-4}$ s in $\mathrm{Bi_6O_4(OH)_4}^{6+}$ [44] and $\tau \approx 0.1$ s in $\mathrm{Rh(H_2O)_6}^{3+}$ [31].

A strong acetone coordination to the Zr tetramer has been observed, similar to the situation in, for example, aqueous solutions of Rh(III) [31]. In view of the popularity of the method of adding acetone (or other solvents) to aqueous solutions [e.g. 12] these results should be taken as a warning, especially for studies involving hard, highly charged metal ions.

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