Periodates of Tetravalent Titanium, Zirconium, Hafnium and Thorium: Synthesis, Characterisation and EXAFS Study

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Reaction of $TiO(SO_4)\cdot xH_2O$ with periodic acid in aqueous solution at pH = 2 yields a precipitate of $Ti_2O_2HIO_6\cdot 5H_2O$, while reaction of zirconyl, hafnyl or thorium nitrate with periodic acid in hot aqueous nitric acid solutions yields $MHIO_6\cdot xH_2O$ (M = Zr, Hf, Th; x = 4 or 5). The thorium periodate is soluble in aqueous KOH and $KThIO_6\cdot 4H_2O$ can be precipitated from these solutions. The zirconium, hafnium and both thorium periodates are shown by EXAFS to consist of edge-sharing chains of MO_8 and IO_6 units, IR and Raman studies indicate protonation of periodate in the $MHIO_6$ modifications. The titanium periodate contains vertex-sharing IO_6 groups.

Introduction

Polyoxometalates of electropositive metals have a number of interesting properties. For example, zirconium phosphates can be produced with microporous or mesoporous structures and have potential uses in ion exchange, intercalation, ion conductivity, catalysis and molecular sorption.[1–3] Polymeric structures are found for many oxo anion compounds of Ti, Zr, Hf and Th. Periodate anions $[H_{5-n}IO_6]^{n-}$ function as strong O-donor ligands towards many metal ions of the p and later d blocks, often stabilising unusually high oxidation states, for example Pd^{IV}, Ni^{IV}, Ru^{VI}, Pb^{IV}, Tl^{III} or Cu^{III}.[4–8] In contrast, their compounds with early d-block metals are relatively little investigated.[4] In the case of the oxophilic M^{IV} ions of the group 4 metals (Ti, Zr, Hf) the brief mentions of periodate species in the literature are over 50 years old and contain only compositions derived from classical "wet" analyses, leading to rather unlikely formulations $7TiO_2\cdot I_2O_7$, and $(ZrO_2)_n\cdot I_2O_7\cdot xH_2O$ (x = 3, 4 or 6).[9,10] In the f-block tetravalent thorium is also reported to form periodate complexes.[9,11] The orange cerium(IV) compounds $CeHIO_6\cdot 4H_2O$ and $M'CeIO_6\cdot xH_2O$ (M′ = K, Rb or Cs) were described in the older literature[4,9] and have more recently[12] been characterised by IR and UV/Vis spectroscopy and possible structures proposed based upon extended X-ray absorption fine structure (EXAFS) data from these amorphous and insoluble solids. There are also reports of the stabilization of Tb^{IV} in periodate media.[14,15] Recently, open-framework uranyl periodate compounds have been described,[13] showing the potential to produce useful porous materials with electropositive metals. We report here an investigation of the periodate complexes of these early d-block metals in the oxidation state IV and some experiments on the f-block systems.

Results and Discussion

The products we obtained from the reaction of periodic acid or alkali metal periodates with various group 4 metal reagents proved to be insoluble in water except at very low and sometimes at high pH, amorphous by powder X-ray diffraction (PXD) and often of variable composition. In large part, this is a result of the complex and only partially understood solution chemistry of the group 4 M^{IV} ions in which oxo- or hydroxo-bridge oligomeric hydrolysis products are common features.[16,17] Often this results in rather intractable chemistry. Our general approach was to carry out a variety of exploratory syntheses, examine the products formed by energy dispersive X-ray analysis (EDX) to establish the elements present and their ratios, and use IR spectroscopy to examine the form ($[IO_4]^-$ or $[H_{5-n}IO_6]^{n-}$) of any periodate present.[4] Preparations which yielded species of reproducible composition and which were homogeneous by EDX (spectra collected on a series of points) were selected for detailed study.

Titanium

The addition of $TiCl_4$ to aqueous solutions of H_5IO_6, boiling freshly precipitated titanium dioxide with aqueous H_5IO_6, or reaction of $TiCl_4$ dissolved in glacial acetic acid with H_5IO_6 and KNO_3 in water (the last gave $KM''IO_6$ for M′′ = Ge or Sn[7]), formed white precipitates which contained only small amounts of iodine (EDX evidence) and

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were mainly the hydrated dioxide. Similarly, heating freshly precipitated TiO_2 with H_5IO_6 or H_5IO_6/KIO_4 in water in hydrothermal bombs at ca. 150 °C for 3–4 d gave products containing very little iodine (the temperatures are limited by the stability of H_5IO_6 which decomposes above ca. 175 °C[18]). The addition of concentrated aqueous H_5IO_6 solution to one of $TiOSO_4 \cdot xH_2O$ in hot aqueous H_2SO_4 or to a solution of freshly precipitated TiO_2 in hot aqueous nitric acid was more successful, producing white precipitates of constant composition. If carried out as described in the Exp. Sect. at pH = 2, after washing with water and prolonged drying in vacuo, the products have a reproducible heavy atom ratio of Ti/I = 2:1 and conventional analysis data are consistent with a composition $Ti_2O_2HIO_6 \cdot 5H_2O$. The thermogravimetric analysis (TGA) trace (Figure 1) is very simple, the first weight loss ($<$ 200 °C) corresponding to $-5H_2O$, and the second to –"HIO_4", which is complete at ca. 700 °C leaving TiO_2 (identity confirmed by PXD).

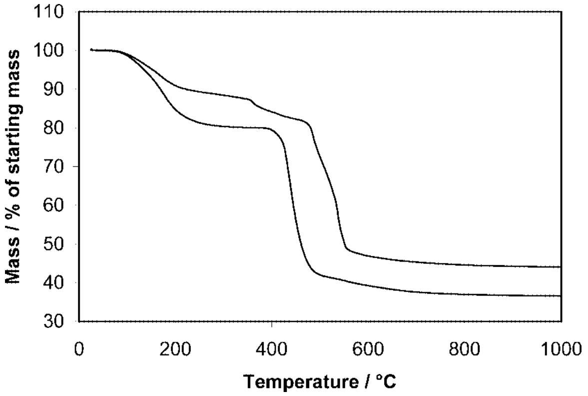

Figure 1. TGA traces of $ThHIO_6 \cdot 5H_2O$ (top) and $Ti_2O_2HIO_6 \cdot 5H_2O$ (bottom) recorded in oxygen.

If the reactions are carried out at higher pH, for example by adding KOH/KIO_4 solution to the acid solution of titanium, the white precipitates have variable composition and presumably are mixtures containing titanium dioxide. In the reactions carried out in the presence of KIO_4, or if the isolated product is treated with 2 M KOH solution no potassium is incorporated. The white powder $Ti_2O_2HIO_6 \cdot 5H_2O$ is insoluble and unaffected by water, dissolves in concentrated aqueous nitric or perchloric acids, and is decomposed by 10 M KOH on heating with precipitation of titanium dioxide.

The IR spectrum of this material shows vibrations due to H_2O, "IO_6" groups and a weak feature at 1135 cm^{-1} assigned to δ(IOH)[4] consistent with the protonation of the periodate required by charge balance. The spectral profile is similar to those found in other complexes containing HIO_6^{4-} species.[4,5] The low-frequency region is dominated by the strong broad absorptions of the coordinated periodate group and these probably obscure features due to Ti–O–Ti units. The compound fluoresces in the Raman spectrometer and this limits the spectral quality, but in addition to strong features at 791 (sh), 654 and 476 cm^{-1} associated with the periodate groups, there is a medium-intensity feature at 936 cm^{-1} which may be due to a Ti–O–Ti unit. The diffuse reflectance spectrum shows a broad feature in the near UV at ca. 36000 cm^{-1} which is tentatively assigned as overlapping internal absorptions of the coordinated periodate ligand and $O \rightarrow Ti^{IV}$ charge transfer (CT). The $Ti_2O_2HIO_6 \cdot 5H_2O$ is amorphous but some structural data were obtained by iodine-*K* edge EXAFS studies (see EXAFS section).

Zirconium and Hafnium

Reactions similar to those described for titanium, including attempted reactions of the freshly precipitated dioxides with H_5IO_6 in hydrothermal bombs or with refluxing aqueous H_5IO_6 failed to give periodato compounds. However, the addition of a concentrated aqueous periodic acid solution to a solution of zirconyl nitrate, $ZrO(NO_3)_2 \cdot xH_2O$, in hot aqueous nitric acid, produced a white precipitate with a Zr/I = 1:1 composition. The hafnium analogue was obtained similarly using $HfO(NO_3)_2 \cdot xH_2O$.[19] Provided the precipitation occurs at pH ≈ 2 and the products are washed thoroughly with hot water and dried in vacuo at room temperature to constant weight, they had a reproducible composition of $MHIO_6 \cdot xH_2O$. These materials were found to be amorphous by PXD but homogeneous by EDX over a series of points. Both the conventional analyses and the TGA weight loss suggest that the thoroughly dried compounds have $x = 4$ for Zr and 5 for Hf. The differences between the two formulations are small but greater than the experimental uncertainty and are reproducible, although we cannot rule out that the water content may be slightly variable. As observed with titanium, working at a higher pH seems to lead to products containing appreciable amounts of the dioxides, and if preparations are carried out in the presence of KIO_4, or the freshly isolated $MHIO_6 \cdot xH_2O$ is treated with 2 M KOH, no significant amount of potassium is incorporated. In contrast to the titanium periodate described above, the compounds $MHIO_6 \cdot xH_2O$ dissolve in 10 M aqueous KOH to give a clear solution, but the white products precipitated from these solutions by addition of ethanol had a highly variable K/I/M ratio and have not been purified or identified. The compounds $MHIO_6 \cdot xH_2O$ are amorphous, insoluble in water, but dissolve in concentrated HNO_3 or $HClO_4$. Their IR spectra show water, "IO_6" groups and a weak broad feature at 1150–1165 cm^{-1} assigned as δ(IOH). If the samples are treated with D_2O for 48 h, the IR spectra of the products show this band has diminished in intensity and a new feature at ca. 820 cm^{-1} is present assigned as δ(IOD). The Raman spectra of the two compounds (Figure 2) are very similar showing only small variations in relative band intensities and frequencies suggesting similar structural units present. The TGA data show decomposition to MO_2 at ca. 650 °C.

For many later transition metal ions, the periodate complexes have related tellurate analogues (containing $[H_{6-n}TeO_6]^{n-}$ ligands[4]), but addition of telluric acid to solutions of Zr^{IV} or Hf^{IV} in nitric acid under the conditions

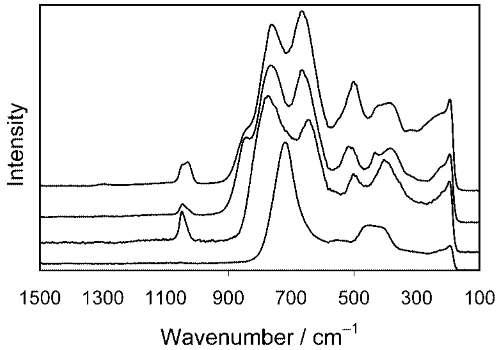

Figure 2. Raman spectra of (top to bottom) $ZrHIO_6{\cdot}4H_2O$, $HfHIO_6{\cdot}5H_2O$, $ThHIO_6{\cdot}5H_2O$ and $KThIO_6{\cdot}4H_2O$.

used to prepare the periodates gave no precipitation. It seems probable that the weaker telluric acid is fully protonated at these pH values and does not coordinate to the group 4 metal.

Thorium

Thorium(IV) is much less prone to hydrolysis and oligomerisation in aqueous solution than the group 4 metal ions, and treatment of aqueous thorium nitrate solution with an aqueous H_5IO_6 solution in the pH range 2–4 produces a white precipitate of composition $ThHIO_6{\cdot}5H_2O$. The IR and Raman spectra of this compound are very similar to those of the Zr and Hf compounds suggesting related structural units. The compound dissolves in concentrated mineral acids and in strong aqueous alkali solution. The TGA plot showing thermal decomposition to ThO_2 (Figure 1) is simple, showing water loss in two steps and then loss of "HIO_4" with no other intermediates formed.

When $ThHIO_6{\cdot}5H_2O$ is stirred with 5 M KOH solution, it slowly dissolves to give a colourless solution, from which slow addition of ethanol precipitates a white powder identified by analysis as $KThIO_6{\cdot}4H_2O$. The IR and Raman spectra of this product (Figure 2 and Exp. Sect.) are clearly different to that of $ThHIO_6{\cdot}5H_2O$, in particular the "IO_6" region is simpler and the weak features attributed in the latter to δ(IOH) modes are absent. The compound is amorphous and insoluble in water, except at very low pH. The behaviour of $ThHIO_6{\cdot}5H_2O$ in alkali is reminiscent of that of $CeHIO_6{\cdot}4H_2O$,[12] and contrasts with that of the Zr and Hf systems.

Cerium, Praseodymium and Terbium

Reaction of $[NH_4]_2Ce(NO_3)_6$ in aqueous HNO_3 with periodic acid precipitates deep yellow $CeHIO_6{\cdot}4H_2O$;[12] this can also be prepared from cerium(III) ions and periodic acid oxidised with ozonised oxygen[12] and (impure) from cerium(III) nitrate and aqueous periodic acid.[20] Since stable and soluble Pr^{IV} or Tb^{IV} precursors are unavailable, ozonisation of aqueous Pr^{III} and Tb^{III} nitrate solutions containing H_5IO_6 at pH = 2 was explored, but even after several hours there was no evidence for oxidation of the lanthanide (in situ UV/Vis spectra). There are several reports[14,15,21–24] that in alkaline solution at least partial conversion to the M^{IV} state is possible, either electrochemically or by using strong chemical oxidants such as peroxodisulfate or ozone. If $Pr(NO_3)_3$ solution is added dropwise to a 5 M KOH solution containing KIO_4, through which ozonised oxygen is passing, a brown colour appears and after several hours a deep yellow solution with a yellow-brown precipitate is formed. The UV/Vis spectra of the yellow solution is dominated by a strong broad band at ca. 34000 cm^{-1}, similar in energy to features reported for other Pr^{IV} species and assigned as O → Pr^{IV} CT.[21] The yellow solution decomposes slowly producing a white precipitate and a green solution of Pr^{III}. Filtration and addition of saturated KNO_3 solution to the filtrate produced a fawn-yellow precipitate which became darker on drying. EDX data on this precipitate showed it contained K, I and Pr but was inhomogeneous. The IR spectrum is similar to that of $KCeIO_6{\cdot}xH_2O$.[12] Once isolated, the material is insoluble in water or aqueous alkali and decomposes to green Pr^{III} instantly by acids. The solid decomposes to green Pr^{III} over a few hours/days. Similar ozonisation of a solution of $Tb(NO_3)_3$, KOH and KIO_4 produced a deep red brown solution and a brown precipitate. Filtration and addition of saturated aqueous KNO_3 to the filtrate gave a red-brown solid. EDX data on this solid showed K, Tb and I, although again the ratios differed from sample to sample. The IR spectrum showed water and "IO_6" and the UV spectrum, both of the original red-brown solution and the isolated solid, contained a strong broad feature at ca. 25500 cm^{-1} assigned as O → Tb^{IV} CT. Formation of Tb^{IV} in periodate media has been reported several times before[15,22] and Ying and Rudong[15] claimed the isolation and characterisation of $MTbIO_6{\cdot}xH_2O$ (M = Li, x = 14; M = Na, x = 7; M = K, x = 8) complexes by this route. Our spectroscopic data are in good agreement with those reported, but despite very many attempts we have been unable to obtain species which have a constant composition or are homogeneous.

We conclude that substances which probably contain $KMIO_6{\cdot}xH_2O$ (M = Pr or Tb) analogous to the cerium complex do form, but it is very doubtful if they can be obtained even approximately pure, and this precludes work to establish the structural units present.

EXAFS Studies

All the tetravalent periodate materials discussed herein are amorphous; all attempts to produce crystalline materials by varying the synthesis conditions and hydrothermal growth failed. The EXAFS study was undertaken with the aim of discovering some information about their local structures. EXAFS data were recorded at both the metal (Zr-K, Hf-L_{III}, Th-L_{III}) and iodine (K) edges for $MHIO_6{\cdot}xH_2O$ (M = Zr, Hf, Th) and $KThIO_6{\cdot}4H_2O$. For $Ti_2O_2HIO_6{\cdot}5H_2O$, only iodine-K edge data were recorded since the titanium-K edge lies in the iodine-L region.

The iodine edge spectra of $ZrHIO_6{\cdot}4H_2O$ were fitted readily with a first shell of 6 oxygen atoms at a distance of 1.88 Å. A second shell was clearly visible in the Fourier transform at 3.27 Å and this could be fitted, with very similar statistics, with one or two zirconium atoms. A larger number of zirconium atoms resulted in deterioration of the fit statistics. The zirconium EXAFS contained a strong first shell at 2.18 Å. This shell gave a poor fit with six oxygen atoms which improved markedly with eight-coordination. The fit with seven-coordinate Zr was indistinguishable from the eight-coordinate model. A second shell at 3.26 Å was modelled with two iodine atoms, similarly to the iodine data, a single iodine atom gave a reasonable fit but a larger number did not. The background-subtracted spectra and Fourier transforms are shown in Figure 3 and structural data are presented in Table 1.

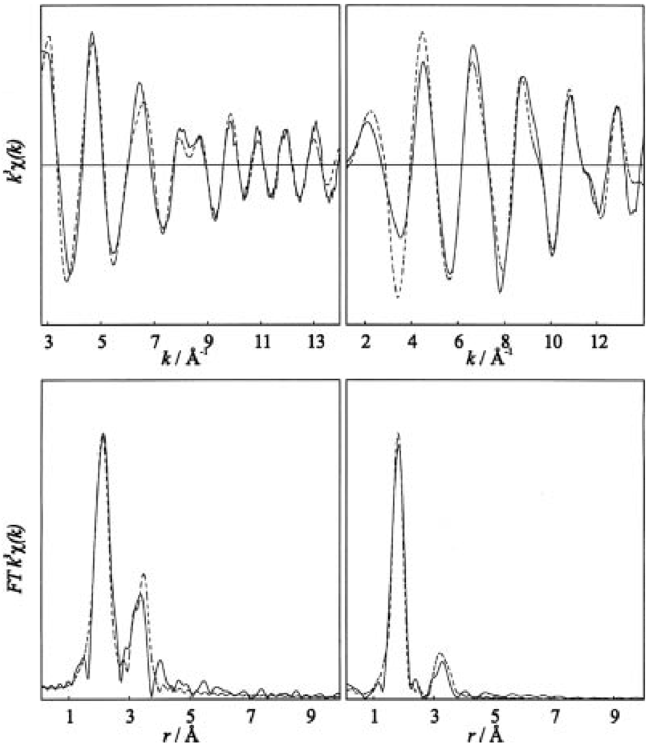

Figure 3. Fitted zirconium- (left) and iodine-K (right) edge EXAFS (top) and Fourier transformed EXAFS (bottom) spectra of $ZrHIO_6{\cdot}4H_2O$. Experimental data is shown as solid lines and calculated spectra as broken lines.

Table 1. EXAFS data for $MHIO_6{\cdot}xH_2O$ (M = Zr, Hf, Th) and $KThIO_6{\cdot}4H_2O$ (the calculated standard deviations are from the EXAFS fitting software and a 1% error in the distances should be considered more reasonable).

			Metal edge EXAFS (Zr-K, Hf-L_{III}, Th-L_{III})[a]			
M	M–O [Å]	σ^2	M···I [Å]	σ^2	E_F	R (%)
Zr	2.177(6)	0.023(1)	3.261(5)	0.012(1)	–1.4	26.0
Hf	2.15(2)	0.035(3)	3.22(2)	0.017(6)	–8.9	32.4
Th	2.46(1)	0.029(2)	3.501(8)	0.012(1)	–6.7	33.9
KTh	2.46(2)	0.014(3)	3.54(1)	0.010(2)	–6.8	47.2
			I-K edge EXAFS[b]			
M	I–O [Å]	σ^2	I···M [Å]	σ^2	E_F	R (%)
Zr	1.875(4)	0.007(1)	3.267(5)	0.011(2)	–14.3	28.2
Hf	1.863(4)	0.009(1)	3.25(3)	0.015(3)	–11.4	26.2
Th	1.844(7)	0.011(2)	3.41(2)	0.010(3)	–8.9	34.8
KTh	1.868(9)	0.007(2)	3.5(3)	0.05(12)	–10.7	27.0

[a] Coordination numbers: M–O = 8; M···I = 2. [b] Coordination numbers: I–O = 6; I···M = 2.

The Zr···I distances observed in both the Zr and I edge data are consistent with edge-sharing polyhedra, with a Zr–O–I bond angle of 108°. Based on this and the observed coordination numbers, two structural models for $ZrHIO_6{\cdot}4H_2O$ are plausible based on this EXAFS data. The first is that chains are formed with alternating IO_6 and ZrO_8 groups; this is the case if the second shell in both data sets is modelled with two atoms. The second model arises from the possibility of a single atom in the second shell and would give rise to dimeric species containing a periodate ion and one zirconium atom. This second model does not fit with the insolubility of the material, but more importantly is not plausible due to the composition. In the chain model the edge-sharing periodate ions fill four coordination sites on Zr, the remaining four can be occupied by water molecules (probably hydrogen-bonded to neighbouring chains). With dimers, six water molecules would be needed for ZrO_8. Seven-coordinate Zr is also consistent with the EXAFS data, but this would still require five water molecules. Thus, edge-sharing chains with alternating ZrO_8 and IO_6 groups (Figure 4) is considered the most likely structure of this material.

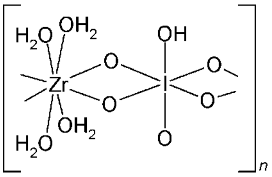

Figure 4. Proposed structural motif in $ZrHIO_6{\cdot}4H_2O$.

The EXAFS data quality for $HfHIO_6{\cdot}5H_2O$, $ThHIO_6{\cdot}5H_2O$ and $KThIO_6{\cdot}4H_2O$ was poorer than for the Zr system discussed above. The Hf-L_{III} edge data was noisy and had to be truncated; only 1.5–9 Å^{-1} were used, but it was possible to obtain meaningful information from these data, albeit with slightly high R factors. The Th-L_{III} edge data suffered with two major monochromator glitches and the relevant data points were deleted. Similarly, a major glitch in the iodine edge EXAFS data, which was not observed in the other samples, became apparent in both Th samples and a section had to be cut from the data. This has resulted in high R factors for the Th data at both edges and unreliable second-shell information in the I-K edge fits.

Examination of the data in Table 1 shows that $HfHIO_6{\cdot}5H_2O$ is very similar to $ZrHIO_6{\cdot}4H_2O$ and the same structure appears to be adopted. The small reduction in the M–O distance is consistent with ionic radii[25] and the agreement between the Hf···I and I···Hf distances, though poorer than with Zr, is still within error. The M–O bond lengths for the Zr and Hf compounds are in excellent agreement with those in the $[M_4(OH)_8(H_2O)_{16}]^{8+}$ ions.[17] Interestingly, even accepting their lower reliability, the fits to the data collected on the protonated and potassium-exchanged thorium periodates are also compellingly similar to $ZrHIO_6{\cdot}4H_2O$. The first-shell distance increase for Th compared with Zr is slightly larger than the 0.21 Å suggested by ionic radii and this could be taken to imply nona-coordinate Th in $ThHIO_6{\cdot}5H_2O$, though the distance is the same in $KThIO_6{\cdot}4H_2O$ where the number of water molecules is insufficient for nona-coordinate Th. The EXAFS data of $ZrHIO_6{\cdot}4H_2O$ is also markedly similar to that of $CeHIO_6{\cdot}4H_2O$.[12] The chain structure which we consider likely here was also proposed in this earlier work, though it was only possible to fit one shell to the Ce EXAFS data and the chain structure was based on the iodine edge data only. Thus, we suggest that the same core structure is adopted throughout the series of tetravalent periodates with these electropositive metals containing $ZrHIO_6{\cdot}4H_2O$, $HfHIO_6{\cdot}5H_2O$, $CeHIO_6{\cdot}4H_2O$, $ThHIO_6{\cdot}5H_2O$ and $KThHIO_6{\cdot}4H_2O$. The fifth water molecule observed in some of these compounds is likely to be loosely associated. The potassium ion in $KThIO_6{\cdot}4H_2O$ does not appear to change the EXAFS data at either edge, but in all the metal edge spectra there are features in the Fourier transform beyond the second shell which have not been modelled. Vertex-sharing potassium would be in this region. The Raman spectra of the thorium compounds (Figure 2) show the change in the symmetry of the periodate ion on exchange of the proton in $ThHIO_6{\cdot}5H_2O$ with potassium to yield $KThIO_6{\cdot}4H_2O$ and are consistent with an increased symmetry on deprotonation but an otherwise similar environment.

The iodine-*K* edge data for $Ti_2O_2IO_6{\cdot}5H_2O$ were fitted (R = 20.92) with six oxygen atoms at 1.861(3) Å and two titanium atoms at 3.51(2) Å; Debye–Waller factors were 0.006(1) and 0.014(5) Å^2, respectively. Whilst the information which can be derived from one edge is clearly less, it is possible to see that this material is structurally different from those described above. Assuming a typical octahedral Ti^{IV}–O distance of 1.97 Å, the Ti–O–I bond angle would be around 133°; thus, it is likely that the structure of this material is based around vertex-sharing polyhedra. A second shell with more than two titanium atoms does not give a good fit, ruling out higher symmetry structures, and there are not enough oxide/hydroxide/water groups for a discrete molecular structure. Hence, a structure based on chains or sheets is likely.

Experimental Section

General: Physical measurements were made as described previously.[5] For analysis known weights of the compounds were boiled with 2 M H_2SO_4 and excess aqueous SO_2 which achieved dissolution and reduction to iodide. Iodine was determined gravimetrically as AgI and potassium gravimetrically as $KBPh_4$, and the group IV metals and Th as the dioxides by pyrolysis to constant weight in flowing O_2/N_2. Water contents were estimated from the TGA traces. All samples were examined by PXD and found to be fully amorphous. X-ray absorption data were collected at ambient temperature in transmission mode from powdered samples diluted with BN on station 9.3 of the SRS with an Si 220 monochromator. Background subtraction was performed with PAXAS[26] and EXAFS data were fitted using EXCURVE.[27] $ZrO(NO_3)_2{\cdot}xH_2O$, $TiO(SO_4){\cdot}xH_2O$, $Pr(NO_3)_3{\cdot}xH_2O$ and $Tb(NO_3)_3{\cdot}xH_2O$ (Aldrich), and $Th(NO_3)_4{\cdot}5H_2O$ (BDH), were used as received. $HfO(NO_3)_2{\cdot}xH_2O$ was prepared as described elsewhere.[19]

$Zr[HIO_6]{\cdot}4H_2O$: $ZrO(NO_3)_2{\cdot}xH_2O$ (0.26 g, ca. 1.0 mmol) was dissolved in hot aqueous nitric acid (5:1 v/v, H_2O/HNO_3, 200 mL) and the solution stirred vigorously, whilst a solution of H_5IO_6 (0.34 g, 1.5 mmol) in water (20 mL) was added dropwise. Immediately, a white precipitate formed, and after stirring for 30 min the hot solution was filtered, the solid washed with hot water (3 × 50 mL) and dried in vacuo for 24 h (0.35 g, 90%). $H_9IO_{10}Zr$ (387.19): calcd. I 32.8, Zr 23.6; found I 33.3, Zr 23.8. IR (Nujol): $\tilde{\nu}$ = 3380 (st, br), 1624 (m), 1153 (w), 780 (sh), 720 (vs), 494 (s), 379 (m) cm^{-1}. Raman: $\tilde{\nu}$ = 3300 (w, br) 1580 (w), 1038 (m), 825 (sh), 761 (vs), 662 (vs), 502 (m), 381 (m), 192 (m) cm^{-1}. UV/Vis (neat diffuse reflectance): $\tilde{\nu}$ = 45450, 35700, ca. 33000 (sh) cm^{-1}.

$Hf[HIO_6]{\cdot}5H_2O$: This compound was prepared similarly using $HfO(NO_3)_2{\cdot}xH_2O$. Yield 86%. $H_{11}HfIO_{11}$ (492.48): calcd. Hf 36.2, I 25.8; found Hf 35.8, I 24.9. IR (Nujol): $\tilde{\nu}$ = 3380 (st, br), 1615 (m), 1161 (w), 760 (sh), 720 (vs), 502 (s), 379 (m) cm^{-1}. Raman: $\tilde{\nu}$ = 3300 (w, br), 1580 (w), 1036 (m), 844 (sh), 765 (vs), 666 (vs), 514 (m), 434 (m), 381 (m), 194 (m) cm^{-1}. UV/Vis (neat diffuse reflectance): $\tilde{\nu}$ = 45450, 35700, ca. 34000 (sh) cm^{-1}.

$Th[HIO_6]{\cdot}5H_2O$: Thorium nitrate hydrate (0.24 g, 0.48 mmol) was dissolved in water (20 mL), concd. HNO_3 (1 mL) added and the mixture heated to ca. 80 °C. A solution of H_5IO_6 (0.15 g, 0.65 mmol) in water (10 mL) was added and the mixture stirred for 30 min. The white precipitate was filtered off, rinsed with hot water (3 × 20 mL) and dried in vacuo (0.22 g, 85%). $H_{11}IO_{11}Th$ (546.02): calcd. I 23.2, Th 42.5; found I 23.8, Th 42.4. IR (Nujol): $\tilde{\nu}$ = 3380 (st, br), 1620 (m), 1161 (w), 760 (sh), 725 (vs), 447 (s), 370 (m) cm^{-1}. Raman: $\tilde{\nu}$ = 3300 (w, br), 1580 (w), 1040 (m), 772 (vs), 640 (vs), 498 (m), 396 (m), 200 (m) cm^{-1}. UV/Vis (neat diffuse reflectance): $\tilde{\nu}$ = 44800, 36000 cm^{-1}.

$Ti_2O_2[HIO_6]{\cdot}5H_2O$: Powdered $TiO(SO_4){\cdot}xH_2O$ (1.6 g, 10 mmol) was suspended in hot water (300 mL) and the mixture vigorously stirred whilst aqueous ammonia (25% w/v, 10 mL) was added, producing a flocculent white precipitate. The mixture was boiled for 10 min, then filtered hot and the white solid washed with copious amounts of hot water to remove residual ammonia. The wet solid was added to a hot mixture of water and concd. nitric acid (4:1 v/v, 100 mL), where it dissolved slowly on stirring to give a clear solution. Periodic acid (2.3 g,10 mmol) in water (10 mL) was added to this solution resulting in a white precipitate. After 10 min, the precipitate was filtered off, washed with hot water (3 × 20 mL) and dried in vacuo. (1.8 g, 82%). $H_{11}IO_{13}Ti_2$ (441.72): calcd. I 28.7, Ti 21.7; found I 28.5, Ti 21.9. IR (Nujol): $\tilde{\nu}$ = 3300 (st, vbr), 1625 (m), 1135 (m), 890 (sh), 730 (s, br), 473 (s), 370 (m) cm^{-1}. Raman: $\tilde{\nu}$ = 936 (m, sh), 791 (s, sh), 654 (vs), 476 (s), 294 (s) cm^{-1}. UV/Vis (neat diffuse reflectance): $\tilde{\nu}$ = 44000, 35800 cm^{-1}.

$KThIO_6{\cdot}5H_2O$: $Th[HIO_6]{\cdot}5H_2O$ (0.2 g, 0.37 mmol) was suspended in 5 M KOH (10 mL) and stirred for 1 h, where it dissolved to give a clear solution. Ethanol (20 mL) was added dropwise to the rapidly stirred solution producing a white precipitate. This was filtered off, washed with ethanol/water (1:1 v/v, 20 mL) and dried in vacuo (0.18 g, 86%). $H_{10}IKO_{11}Th$ (584.11): calcd. I 22.3, K 6.7; found I 22.4, K 6.8. IR (Nujol): $\tilde{\nu}$ = 3350 (st, br), 1640 (m), 698 (vbr, s), 668 (sh), 440 (br, m) cm^{-1}. Raman: $\tilde{\nu}$ = 3300 (w, br), 1580 (w), 720 (vs), 540 (m), 466 (br, m), 200 (m) cm^{-1}.

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