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Structure of Tetrameric Aqua Ruthenium(IV): an Investigation by Ruthenium K Edge EXAFS

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Introduction

Red-brown aqueous Ru^{IV} has been known since the 1950s.[1] Methods for its preparation have involved H_2O_2 reduction of RuO_4,[2] reaction of $[RuBr_6]^{2-}$ with BrO_3^-,[3] and anodic oxidation of solutions of $[Ru(OH_2)_6]^{2+}$ (or $Ru(OH_2)_6]^{3+}$).[4] In each case solutions are prepared in a noncomplexing acidic medium such as $HClO_4$, and, provided they are kept below pH 1, they are stable for long periods (months) but slowly deposit hydrous RuO_2 as the pH is raised. Early arguments were put forward in favor of mononuclear RuO^{2+}(aq) (or $Ru(OH)_2{}^{2+}$(aq))[2] or dinuclear[5] species. The tetranuclear formulation is now generally agreed on the basis of electrochemical results (reduction to $Ru^{3.75+}$ and $Ru^{3.25+}$ [6,7] and oxidation to $Ru^{4.25+}$ [8] valence states), charge/metal determinations using cation-exchange chromatography[2,7] and Donnan membrane equilibration studies.[9] The existence of tetranuclear $Ru_4O_6{}^{n+}$ complexes has moreover been suggested in the extensive Russian literature[10] largely on the basis of careful analytical and spectroscopic data.

In 1991 we reported isolation and spectroscopic characterization of a complex obtained following treatment of solutions of Ru^{IV}(aq) at pH 2 with potassium hydridotris(pyrazol-1-yl)borate ($KHBpz_3$).[4] In the continuing absence of a single-crystal X-ray structure, +ve ion FAB mass spectral and elemental analysis supported a formula, $[Ru_4O_{6-n}(OH)_n(HBpz_3)_4]X_n$ ($X = ClO_4^-$, NO_3^-, $CF_3SO_3^-$) for the complex containing a variably protonated $Ru_4O_6{}^{4+}$ core. Quantitative oxygen-17 NMR studies on an isotopically labeled sample of Ru^{IV}(aq) provided further support for the oxo-bridged $Ru_4O_6{}^{4+}$ core[4] and not the $Ru_4(OH)_{12}{}^{4+}$ core largely represented in a previous articles.[1,2,6−9] In 1991 we proposed two alternative structures, **A** and **B**, for the basic Ru_4O_6 core, Figure 1. The existence of the highly symmetrical adamantanoid structure **A** is supported by the simplicity of the ^{17}O NMR spectrum of labeled Ru^{IV}(aq) consisting of only two lines (coordinated water and μ-oxo).[4] Support for the rectangular "stacked di-μ-oxo dimer" structure **B** comes from the observation that reduction to Ru^{III} readily leads to dimeric products[6] and that several di-μ-oxo Ru^{IV} complexes have been structurally characterized.[11] In the absence as yet of a definitive X-ray structure of the aqua ion, or of an authentic derivative, we report herein the results of a ruthenium K edge EXAFS investigation on solutions of Ru^{IV}(aq) in both perchloric and nitric acid media in the expectation of being able to distinguish between these two possible core structures for the tetranuclear aqua ion.

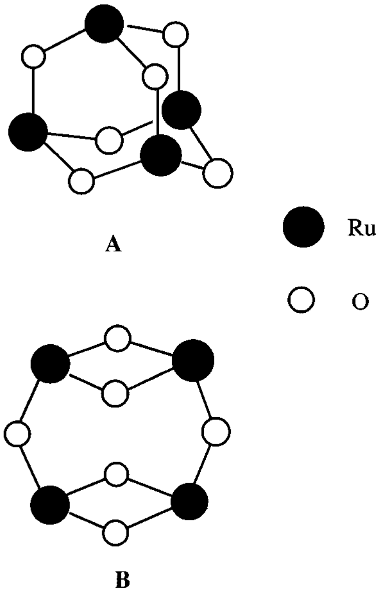

Figure 1. Proposed core structures for Ru^{IV}(aq) based upon existing analytical data (each Ru atom has three coordinated water molecules)

Experimental Section

Preparation of Solutions of Ru^{IV}(aq). Solutions of red-brown aqueous Ru^{IV} were prepared as described previously[4,5] employing the reduction of *in situ* generated RuO_4 extracted into CCl_4 with H_2O_2 in 2M $HClO_4$. Purification from polymeric forms is then carried out using cation-exchange chromatography. In previous investigations[4−7] aqueous Ru^{IV} solutions exchanged onto columns or slurries of Dowex 50W X2 resin (2% cross-linking) 200−400 μm mesh have only been elutable/removable using displacement methods, e.g. with the help of highly charged cations such as Th^{4+} or La^{3+} at pHs ≥ 1. This was previously rationalized as due to protonation of the μ-oxo groups under conditions of attempted acid elution (with >1 M H^+). However we have now found that aqueous Ru^{IV} solutions (up to 10 mM in ruthenium) can be routinely obtained by direct acid elution with 2 M $HClO_4$ or 2M HNO_3 if a column consisting of a more coarse resin matrix (Dowex 50W X2, 50−100 μm mesh) is used. This provided an important step forward since it was highly desirable for the EXAFS measurements to use purified solutions of aqueous Ru^{IV} suitably concentrated without any risk of contamination by other heavy metal ions.

Ruthenium K Edge EXAFS Measurements. Solution samples of aqueous Ru^{IV} (7−10 mM) in 2 M $HClO_4$ or 2 M HNO_3 (0.3 cm^3), prepared as above, were separately loaded into homemade Perspex sample cells constructed with polyester (Mylar) windows.

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(1) (a) Rard, J. A. *Chem. Rev.* **1985**, *85*, 1 and references therein. (b) Wehner, P.; Hindman, J. C. *J. Am. Chem. Soc.* **1950**, *72*, 3911. (c) Niedrach, L. W.; Tevebaugh, A. D. *J. Am. Chem. Soc.* **1951**, *73*, 2385.

(2) Gortsema, F. P.; Cobble, J. W. *J. Am. Chem. Soc.* **1959**, *81*, 5516; **1961**, *83*, 4317.

(3) Deloume, J. P.; Duc, G.; Thomas-David, G. *Polyhedron* **1985**, *4*, 875.

(4) Patel, A.; Richens, D. T. *Inorg. Chem.* **1991**, *30*, 3789.

(5) (a) Atwood, D. K.; DeVries T. *J. Am. Chem. Soc.* **1962**, *84*, 2659. (b) Cady, H. H. *USAEC Rep. UCRL* 1957, 3757.

(6) (a) Schauwers, J.; Meuris, F.; Heerman, L.; D'Olieslager, W. *Electrochim Acta* **1981**, *26*, 1065. (b) D'Olieslager, W.; Heerman, L.; Clarysse, M. *Polyhedron* **1983**, *2*, 1107.

(7) Wallace, R. M.; Propst, R. C. *J. Am. Chem. Soc.* **1969**, *91*, 3779.

(8) Heerman, L.; Van Nijen, H.; D'Olieslager, W. *Inorg. Chem.* **1988**, *27*, 4320.

(9) Wallace, R. M. *J. Phys. Chem.* **1964**, *68*, 2418.

(10) For example: (a) Ginsburg, S. I.; Yuz'ko, M. I., Fomina, T. A.; Evstaf'eva, O. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1975**, *20*, 1082. (b) Orlov, A. M.; Shorikov, Yu. S.; Kunaeva, I. V.; Chalisova, N. N.; Fomina, T. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1979**, *24*, 1373. (c) Vdovenko, V. M.; Lazarev, L. N.; Khvrostin, Ya. S. *Sov. Radiochem. (Engl. Transl.)* **1965**, *7*, 228; **1967**, *9*, 449.

(11) Power, J. M.; Evertz, K.; Henling, L.; Marsh, R.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1990**, *29*, 5058.

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Table 1. Ru K Edge EXAFS-Derived Data: Occupation Numbers (*N*), Interatomic Distances (*D*), and Debye−Waller Factors ($2\sigma^2$)

species		*N*	*D*, Å	$2\sigma^2$, Å^2	*R*, %[a]	FI[a]
Model **A** Adamantanoid (Amplitude Reduction Factor (AFAC) = 0.8)						
Ru^{IV} (aq)	Ru−O(*μ*)	3.10(7)	1.833(2)	0.003	20.4744	0.00032
2 M $HClO_4$	$Ru-OH_2$	2.70(11)	2.163(3)	0.003		
	Ru−Ru	3.00(7)	3.401(17)	0.004		
Ru^{IV} (aq)	Ru−O(*μ*)	3.10(7)	1.837(2)	0.003	25.5070	0.00037
2 M HNO_3	$Ru-OH_2$	3.00(11)	2.163(3)	0.004		
	Ru−Ru	2.90(7)	3.406(2)	0.004		
Model **B** Stacked Dimer (Amplitude Reduction Factor (AFAC) = 0.8)						
Ru^{IV} (aq)	Ru−O(*μ*)	3.00(5)	1.833(2)	0.003	19.7061	0.00022
2 M $HClO_4$	$Ru-OH_2$	2.60(8)	2.167(2)	0.003		
	Ru−Ru (near)	2.40(5)	3.402(1)	0.002		
	Ru−Ru (distal)	0.50(13)	4.436(1)	0.004		
Ru^{IV} (aq)	Ru−O(*μ*)	3.20(7)	1.831(2)	0.004	24.7971	0.00033
2 M HNO_3	$Ru-OH_2$	2.60(10)	2.166(3)	0.002		
	Ru−Ru (near)	2.60(7)	3.405(2)	0.003		
	Ru−Ru (distal)	0.30(23)	4.420(25)	0.006		

[a] $R = \int|\chi^{th}(k) - \chi^{exp}(k)|k^3\,dk/\int|\chi^{exp}(k)|k^3\,dk \times 100\%$,[15] $FI = \sum((k_i)^n(\chi_i^{th} - \chi_i^{exp}))^2$,[15] where χ^{th} and χ^{exp} are the theoretical and experimental EXAFS respectively.

EXAFS spectra were collected on the Wiggler I beam line station 9.2 at the Synchrotron Radiation Source at the UK CLRC Daresbury Laboratory operating at 2GeV and 200mA. The station was equipped with a water cooled harmonic rejecting double crystal Si(220) monochromator and mixtures of argon and helium gas ion chambers for measuring incident (I_o) and transmitted (I_t) beam intensities respectively, and a thirteen-element (TlI/NaI) fluorescence detector. Data were recorded at the ruthenium K edge (22.12 keV) in both transmission and fluorescence mode. The sample temperature was 25.0 ± 0.5 °C.

Data Analysis. In this study all fitting was carried out on the fluorescence data. The raw EXAFS data were processed using the program EXCALIB,[12] and the position of the absorption edge was determined from the derivative of the spectrum using EXBACK.[12] This program was also used to extract the EXAFS function $\chi(k)$ by first-order polynomial removal of the pre-edge data and second- or third-order polynomial removal of postedge data. A k^3 weighting was used to enlarge the oscillations at large *k*. These oscillations ($k^3\chi(k)$) were Fourier transformed to give a quasi-radial distribution function.

Fitting of the structural models **A** and **B** was carried out with the EXCURV92[13] program using curved wave theory with the help of Hedin−Lindquist ground states and von Barth exchange potentials[14] to calculate appropriate phase shifts along with typical Ru−O bond lengths and Ru−Ru distances from crystallographic data.

Results and Discussion

Aqueous Ru^{IV} Solutions. The successful direct acid elution of aqueous Ru^{IV} from columns of Dowex 50W X2 50−100 μm mesh cation-exchange resin with 2 M $HClO_4$ (or HNO_3), reported here for the first time, suggests that the previous immovability from similar columns of Dowex 50W X2 200−400 μm mesh[4,7] may be linked to condensation of tetramer units within the finer grade Dowex beads as a result of greater proximity. The higher cationic charge associated with these condensates may explain why cation displacement, e.g. with La^{3+} (more efficient for highly charged species) but not H^+ displacement, works to remove Ru^{IV}(aq) samples from such fine mesh resin. The tetramer sites are presumed to be more dispersed within the coarser 50−100 μm mesh resin disfavoring condensation and allowing direct acid elution of individual $Ru_4O_6^{4+}$(aq) units at concentration levels (up to 10 mM in ruthenium) suitable for EXAFS using fluorescence detection. For the preparation of higher concentrations of aqueous Ru^{IV} (>10 mM) however the use of cation-exchange displacement at lower acidities remains the only viable method.

Ru K Edge EXAFS. Fits to the unfiltered ruthenium K edge EXAFS data obtained from solutions of Ru^{IV}(aq) in both 2 M $HClO_4$ and 2 M HNO_3 are shown in Table 1 and are illustrated for the case of the 2 M $HClO_4$ solution in Figure 2. The quality of fit is reported relative to the discrepancy index, *R*, and the goodness of fit relative to the fit index, FI.[15] The energy independent amplitude reduction factor (AFAC)[13] is a measure of the proportion of the electrons which contribute to an EXAFS-type scatter. It allows for the reduction in amplitude due to the presence of multiple excitations and is usually set to be in the range 0.7−0.9. During fitting the Debye−Waller factor ($2\sigma^2$) and the occupation number (*N*) were independently refined for each shell.

A satisfactory fit to the EXAFS spectrum of Ru^{IV}(aq) in 2 M $HClO_4$ ($R = 20.4744$, FI 0.00032) is obtained for the adamantanoid structure **A** using a three-shell model comprising two different Ru−O shells and a single Ru−Ru shell. The occupancy number (*N*) for each shell refines close to the values of three expected for each well within the quoted errors. The first Ru−O distance of 1.833(2) Å ($N = 3.10(7)$) is assigned to the bonds between Ru and bridging oxo and the second, with a Ru−O distance of 2.163(3) Å ($N = 2.70(11)$), is assigned to the bonds between Ru and coordinated water. Both of these values correlate well with the values for Ru−(μ)O−Ru and $Ru-OH_2$ bond lengths in typical compounds reported in the literature.[11,16] The third shell comprises a single unique Ru−Ru distance of 3.401(17) Å with $N = 3.00(7)$. A further indication that **A** is a good structural model are the Debye−Waller factors which show the expected increase as the shells move further from the absorbing metal center.

In general, the overall fit improves as the number of shells fitted is increased and this is important toward a consideration of the alternative stacked-dimer model. The significance of a

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(12) Dent, A. J.; Mosselmans, J. F. W. *EPSRC*; Daresbury Laboratory Program Library; Daresbourg Laboratory: Daresbury, UK, 1991.

(13) (a) Binsted, N.; Campbell, J. W.; Gurman, S. J.; Stephenson, P. L. *EPSRC*; Daresbury Laboratory Program Library; Daresbury Laboratory: Daresbury, UK, 1992. (b) Binsted, N.; Strange, R. W.; Hasnain, S. S. *Biochemistry* **1992**, *31*, 12117.

(14) von Barth, U.; Hedin, L. *Int. J. Phys.* **1972**, *C5*, 1629.

(15) Binsted, N.; Evans, J.; Greaves, N. G.; Price, R. J. *Organometallics* **1989**, *8*, 613.

(16) For example: (a) Dengel, A. G.; El-Hendaway, A. M.; Griffith, W. P.; O'Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1990**, 737. (b) Gilbert, J. A.; Eggleton, D. S.; Murphy, W. R., Jr.; Hodgson, D. J.; Meyer, T. J., *J. Am. Chem. Soc.* **1985**, *107*, 3855. (c) Abe, M.; Sasaki, Y.; Yamaguchi, T.; Ito, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1585.

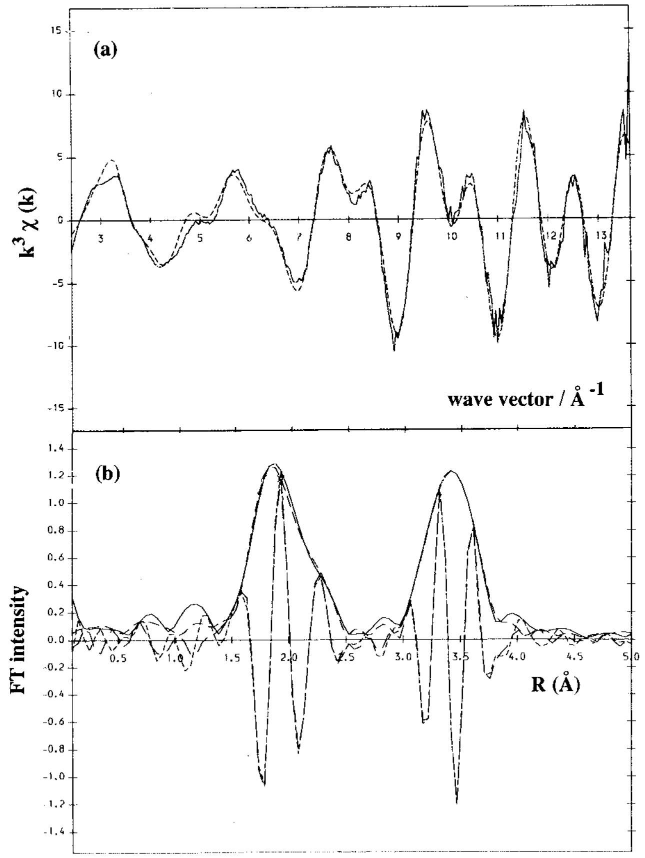
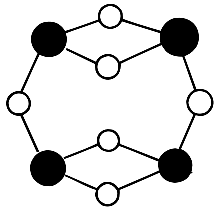


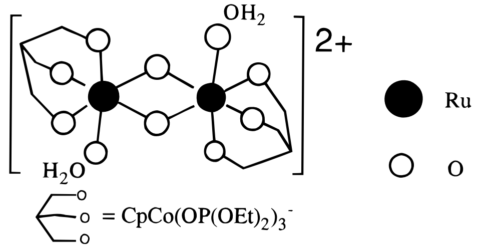
Figure 2. (a) Experimental (—) and calculated (---) EXAFS spectrum from aqueous Ru^{IV} (10 mM) in 2 M $HClO_4$ (phase shifts calculated using Hedin−Lindquist ground states and von Barth exchange potentials). (b) Fourier-transformed (—) experimental and (— — —) calculated and sine-transformed (---) experimental and (— —) calculated EXAFS spectra of aqueous Ru^{IV} in 2 M $HClO_4$.

shell, that is to say the extent to which a particular shell improves the fit, was tested using the statistical package[13] built into EXCURV92. This package was used to test the significance of adding a fourth shell (the distal Ru) in the stacked-di-μ-oxo dimer model **B** with an occupation number of 1.0 while reducing that for the neighboring Ru−Ru shell to 2.0. The results showed that fitting the fourth shell would be significant to a 5% probability level. Despite this, however, attempts to refine the data toward the stacked di-μ-oxo dimer model **B** have proved unsatisfactory in several respects. First, despite the improved fit parameters *R* and FI (expected for the larger number of fitted shells), the refined occupation numbers show large deviations from the required integer values. Those for the most proximal ruthenium atoms refine upward toward 3 (2.4−2.6) with a distance ~3.4 Å rather than the expected value of 2, whereas the value for the single distal ruthenium at ~4.4 Å refines to value significantly below 1 (0.3−0.5). Second, the Debye−Waller factors are randomly distributed for model **B**, Table 1, not exhibiting the expected increase with distance of shell from the absorbing atom. The third shell has a lower Debye−Waller factor than that of the first two shells, but this increases upward as the occupation number for this shell is refined upward toward 3. When fits to the stacked di-μ-oxo dimer model **B** are attempted, it appears that the data always best refines toward the more symmetrical adamantanoid model **A** having three identical proximal rutheniums.

A further feature of the di-μ-oxo bridged structure **B** would be evidence of significant backscattering from a proximal ruthenium atom at a distance of <3 Å. A good model of the di-μ-oxo moiety of structure **B** is the Ru^{IV} dimer complex $[Ru_2O_2(OH_2)_2(L)_2](ClO_4)_2$ (L = $(\eta_5\text{-}C_5H_5)Co(OP(OEt)_2)_3^-$), **C**.[11] Here the Ru−Ru separation is 2.5 Å. The Fourier-transformed EXAFS spectrum of Ru^{IV}(aq), Figure 2, however, clearly contains no significant back-scattering intensity from a neighboring heavy atom in the region between 2.3 and 3.0 Å.



B



C

The stacked di-μ-oxo dimer model **B** should strictly involve fitting to six shells since the two near neighbor rutheniums should be at different distances from the absorbing atom as one is di-μ-oxo bridged and the other mono-μ-oxo bridged. The ruthenium oxygen distances for the two types of bridging oxygen atom will also be different. Attempts to refine a six shell model based on **B** with three unique Ru−Ru and Ru−(μ)O contacts result in negative Debye−Waller factors, irrespective of which ground state and exchange potential values are used, along with *N* values that are too large for the expected number of atoms in each shell. In all cases tried the data refines best toward a highly symmetric model best represented by **A** with only one unique Ru−Ru distance, Figure 2b.

A final piece of evidence arguing against structure **B** for Ru^{IV}(aq) stems from the fact that the di-μ-oxo complex **C**[11] lacks the 480 nm visible absorption band that is characteristic of solutions of aqueous Ru^{IV}, Figure 3, and its known derivatives.[4,6,7]

Having successfully argued for the symmetric three-shell model **A** for Ru^{IV}(aq) based upon the EXAFS data one finally requires to consider the alternative symmetric three-shell model based upon a cuboidal M_4X_4 arrangement. This can immediately be ruled out, however, on the basis of the Ru−(μ)O−Ru angle which can be calculated from the fitted Ru−O(μ) and Ru−Ru distances in Table 1. Such bond angles for oxo-(hydroxo)-bridged cluster compounds with adamantanoid M_4O_6 cores lie in the range 125−140°.[17−22] The cuboidal model,

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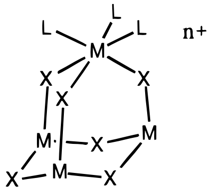
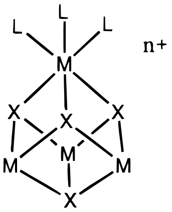
(17) Sala-Pala, J.; Guerchais, J. E.; Edwards, A. E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 870.
(18) Wieghardt, K.; Bossek, U.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 328
(19) Wieghardt, K.; Ventur, D.; Tsai, Y. H.; Kruger, C. *Inorg. Chim. Acta* **1985**, *99*, L25
(20) Wormsbacher, D.; Nicholas, K. M.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1985**, 721.
(21) Glerup, J.; Weihe, H.; Goodson, P. A.; Hodgson, D. J. *Inorg. Chim. Acta* **1993**, *212*, 281.
(22) Wieghardt, K.; Kleine-Boymann, M.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1654.

Table 2. Selected Bond Lengths and Angles for Compounds with Adamantanoid $M_4X_6^{n+}$ and Cuboidal $M_4X_4^{n+}$ Cores (X = O, OH)





M^{n+}	L	M−M (Å)	M−Oav (Å)	M−L (Å)	M−O−M (deg)	ref
Ru^{IV}(aq) 2 M $HClO_4$	H_2O	3.401(17)	1.833(2)	2.163(3)	135.8 (calc)	this work
			Adamantanoid $M_4X_6^{n+}$			
$Ta_4O_6^{8+}$	F^-	3.61	1.93	1.97	139	17
$Mn_4O_6^{4+}$	tacn[a]	3.21(1)	1.79(1)	2.08(1)	128.7(8)	18
$Ti_4O_6^{4+}$	tacn	3.26	1.834	2.23	125.6	19
$Cr_4(OH)_6^{6+}$	π-$C_5Me_5^-$	3.67	1.952(8)		140	20
$Cr_4(OH)_6^{6+}$	tach[a]	3.67	1.973(6)	2.08(1)	136.7	21
$In_4(OH)_6^{6+}$	tacn	3.899	2.144	2.334	130.8	22
			Cuboidal $M_4X_4^{n+}$			
$Ru_4(OH)_4^{4+}$	π-C_6H_6	3.29	2.12	2.23	102.2	23

[a] tacn, 1,4,7-triazacyclononane, tach, 1,3,5-triaminocyclohexane.

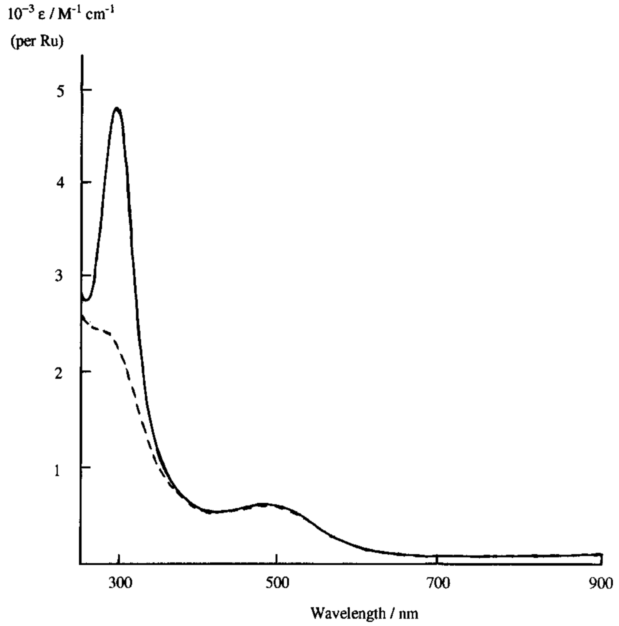


Figure 3. UV−visible absorption spectrum of aqueous Ru^{IV} in (—) 2 M HNO_3 and (---) in 2 M $HClO_4$.

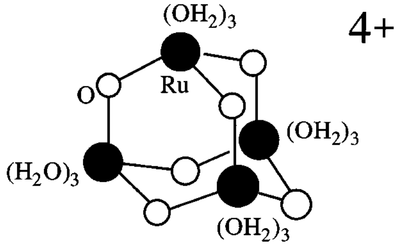


Figure 4. Structure for tetrameric aqueous Ru^{IV} indicated from ruthenium K edge EXAFS.

however, would require a much tighter M−(μ)O−M angle of around 100°.[23] The calculated Ru−(μ)O−Ru angle (135.8°), Table 2, is found to be perfectly consistent with an adamantanoid arrangement but clearly too large to be accommodated within the alternative cube structure.

The EXAFS spectra obtained from Ru^{IV}(aq) solutions in both $HClO_4$ and HNO_3 media are sufficiently similar to confirm the retention of the same structural unit for the tetranuclear core in each case. For the solutions in 2 M HNO_3 fits to the two alternative structures again show that despite the slightly lower *R* value and FI index for structure model **B** the data refines best to the adamantanoid model **A**, Table 1. A feature of interest however is the appearance of an intense UV absorption maximum in the solutions of Ru^{IV}(aq) in 2 M HNO_3 at 303 nm ($\epsilon = 4910\ M^{-1}\ cm^{-1}$) which is absent in the $HClO_4$ solutions, Figure 3, and probably arises from a transition associated specifically with nitrate anion-pair association or inner-sphere coordination of nitrate to the tetrameric cation. The fact that similar concentrations of Ru^{IV}(aq) are elutable using 2 M solutions of either acid and that the band disappears when the nitrate solutions are re-loaded and then eluted with 2 M $HClO_4$ points to the former as being the likely explanation.

In conclusion, the present findings, along with data from previous work, are supportive of the μ-oxo bridged adamantanoid "$Ru_4O_6^{4+}$" core arrangement, Figure 4, for tetrameric aqueous Ru^{IV}. Mononuclear "ruthenyl" and tetranuclear formulations such as $Ru_4(OH)_{12}^{4+}$(aq) can now be unequivocally ruled out as relevant to the core structure of this aqueous ion.

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(23) Gould, R. O.; Jones, C. L.; Robertson, D. R.; Stephenson, T. A. *J. Chem. Soc. Chem. Commun.* **1977**, 222.