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First structural characterization of Pa(IV) in aqueous solution and quantum chemical investigations of the tetravalent actinides up to Bk(IV): the evidence of a curium break†

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More than a century after its discovery the structure of the Pa^{4+} ion in acidic aqueous solution has been investigated for the first time experimentally and by quantum chemistry. The combined results of EXAFS data and quantum chemically optimized structures suggest that the Pa^{4+} aqua ion has an average of nine water molecules in its first hydration sphere at a mean Pa-O distance of 2.43 Å. The data available for the early tetravalent actinide (An) elements from Th^{4+} to Bk^{4+} show that the An-O bonds have a pronounced electrostatic character, with bond distances following the same monotonic decreasing trend as the An^{4+} ionic radii, with a decrease of the hydration number from nine down to eight for the heaviest ions Cm^{4+} and Bk^{4+}. Being the first open-shell tetravalent actinide, Pa^{4+} features a coordination chemistry very similar to its successors. The electronic configuration of all open-shell systems corresponds to occupation of the valence 5f orbitals, without contribution from the 6d orbitals. Our results thus demonstrate that Pa(IV) resembles its early actinide neighbors.

Protactinium, discovered as ^{234m}Pa ($t_{1/2}$ = 1.17 min) in 1913 by Fajans and Göhring in Karlsruhe,[1] is a radioactive metal located between thorium and uranium in the actinide series. ^{231}Pa ($t_{1/2}$ = 3.28·10^4 yr) occurs naturally at low concentrations in uraninite, a uranium-rich mineral. The α-decay of ^{235}U and ^{234}U in sea water produces ^{231}Pa and ^{230}Th, respectively, the ratio of which is used to reconstruct the rates of past ocean circulation.[2] ^{231}Pa is also generated as a byproduct in projected thorium nuclear reactors, making it a contributor to the long-term radiotoxicity of Th-based spent nuclear fuel.[3]

The tetravalent actinide from Th(IV) to Pu(IV) are hard Lewis acids with high charge densities and therefore exhibit a strong tendency to hydrolysis and condensation.[4] However, unlike its neighbor actinides the aqueous chemistry of Pa(IV) is to a large extent unexplored.[5a] This has surely to do with the rarity of the element and its radioactive nature, in addition to the chemical instability of its tetravalent state: Pa(IV) is difficult to stabilize in water due to the low redox potential of the Pa(V)/Pa(IV) couple (-0.1 V/SHE) and the fact that it rapidly oxidizes to Pa(V)[5,6] in comparison, U(IV), Np(IV), and Pu(IV) are more stable. To date, there are no experimental or theoretical studies published on the hydration structure of Pa^{4+} in aqueous solution, while there are several experimental studies on Th^{4+}, U^{4+}, Np^{4+}, Pu^{4+}, and Bk^{4+} mainly by X-ray absorption fine structure (EXAFS).[4a,7] However, such data are absent for Am^{4+} and Cm^{4+}, which are unstable in noncomplexing media.[8] The coordination numbers for the Th^{4+}-Bk^{4+} aqua ions are between eight and thirteen, indicating large uncertainties in their determination, but the corresponding An-O bond distances are obtained with higher precision and are therefore a better measure for the coordination number. This is discussed further in this paper, where we also provide the first EXAFS data on Pa^{4+} in aqueous solution and an effective method that enables a stabilization of Pa(IV) in aqueous solution over several days. Data about the nature of the An-O bond, free energies, and structural trends in the series of An^{4+} aqua ions was gained from quantum chemical calculations on three isomeric clusters, $[An(H_2O)_{10-n}]^{4+}\cdot(H_2O)_n$; n = 0-2; An = Th-Bk, all of which in a dielectric continuum.

Reduction of Pa(V) was initially performed with zinc-mercury amalgam in perchloric, hydrochloric, and sulfuric acid solutions under argon and monitored by UV-vis absorption spectroscopy (see Supplementary Information), where the Pa(IV) buildup was seen as three bands emerging between 220-290 nm due to $5f^1$–$6d^1$ transitions. The re-oxidation of Pa(IV) was rather slow under argon (~30% was converted to Pa(V) in 24 hours) but rapid in air, although the rate depended on the acid and its concentration, being slower in hydrochloric and sulfuric acid than in perchloric acid. Similar observations have been

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reported previously.[5c] The reason for this additional stability is most likely the formation of $PaCl_n^{4-n}$ and $Pa(SO_4)_n^{4-2n}$ complexes that are thermodynamically more stable than the Pa^{4+} aqua ion. Their presence in solution is confirmed by the fact that their absorption bands are red-shifted compared to those of the aqua ion (Fig. 1a).
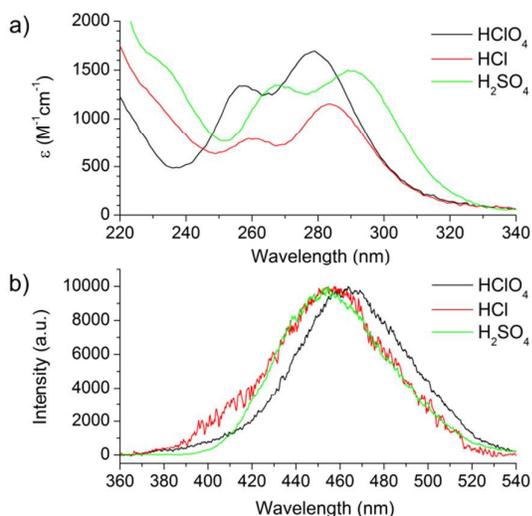
Fig. 1 a) UV-absorption and b) emission spectra (λ_{ex} = 245 nm) of $1.3 \cdot 10^{-5}$ M Pa(IV) in 6 M mineral acids, recorded at 295 K in a 1.0 cm quartz cuvette

A remarkable increase of the Pa(IV) stability was observed by using rongalite ($Na^+HOCH_2SO_2^-$) as reducing agent. As much as 98% Pa(IV) remained after five days in 6 M hydrochloric and sulfuric acid solutions, while in perchloric acid the oxidation rate was significantly higher. It should be noted that rongalite exhibits a rather strong absorption band at 284 nm that masks the Pa(IV) absorption bands (Fig. S1†); thus time-resolved laser fluorescence spectroscopy (TRLFS) was used to study the $6d^1$–$5f^1$ emission spectra of Pa^{4+} in these rongalite-containing solutions. Laser excitation (245 nm) into the 6d levels resulted in a broad emission band at ~465 nm in perchloric acid and ~455 nm in hydrochloric and sulfuric acid, corresponding to Stokes shifts of ~13500 cm^{-1},[5b] slightly larger than ~12500 cm^{-1} observed for the $4f^1$ Ce^{3+} aqua ion (Fig. 1b).[9] While the absorption spectra of Pa^{4+} in hydrochloric and sulfuric acid are red shifted relative to that in perchloric acid, the emission spectra are blue-shifted. In all studied solutions the emission decays were monoexponential, corresponding to luminescence lifetimes of 15-20 ns, not varying notably with the Pa^{4+} concentration or the mineral acid.[5b] Rongalite showed no own emission upon laser excitation at 245 nm, nor did its presence affect the Pa^{4+} emission spectrum (Fig. S2†). Thus we conclude that rongalite does not bind directly to Pa^{4+}, encouraging us to use it to stabilize Pa^{4+} at concentrations suitable for X-ray absorption spectroscopy (XAS).

The structure of the Pa^{4+} aqua ion is preferably studied in dilute acidic aqueous solution with a non-coordinating anion. Although Pa(IV) was found to be stable in perchloric acid and in dilute hydrochloric acid long enough for optical absorption

and luminescence studies, re-oxidation took place in these solutions in the course of the initial XAS studies. Therefore, subsequent studies were performed in 6 M hydrochloric acid where Pa(IV) is more stable. Fig. 2a compares the L_3-edge X-ray absorption near-edge structure (XANES) spectra of the Pa(IV) and Pa(V) solutions. This is the first reported XANES spectrum of aqueous Pa(IV). The white line position of Pa(IV) (16737.3 eV) is about 4 eV lower in energy than that of Pa(V) (16741.5 eV)[10] (Table S1†). The corresponding differences for tetra and pentavalent uranium, neptunium, and plutonium are smaller or even reversed owing to their pentavalent ions present as dioxo actinyl ions in aqueous media, while Pa(V) occurs as a monooxo protactinium cation.[4,11-14] The white line position of the Pa(IV) XANES in 6 M HCl is expected to be only slightly affected by the presence of chloride, as in the case of the XANES data of Np(IV) and Pu(IV) in chloride solutions.[13-14]
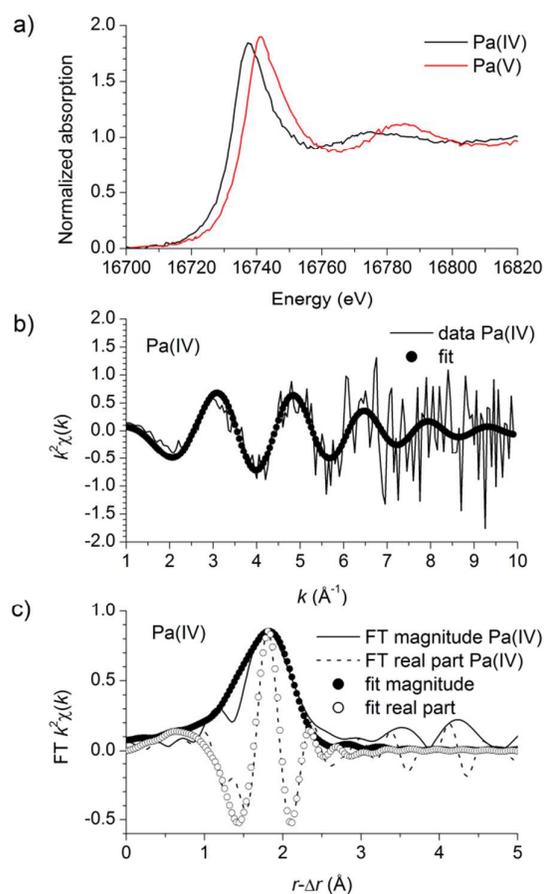
Fig. 2. a) Pa L_3-XANES spectra of 0.3 mM Pa(IV) and Pa(V) in 6 M HCl. b) k^2-weighted EXAFS data with fit and c) Fourier transformed data and fits of 0.3 mM Pa(IV) in 6 M HCl

Consistent structural data of the coordination shell of Pa(IV) was obtained by model fitting of its EXAFS spectrum and Fourier transform (Fig. 2b-c). Two structure models were evaluated: a model with eight oxygen atoms and one chlorine atom in two separate shells (a monochloro complex[15-16]) and a

model with nine oxygen atoms in a uniform backscattering shell. Because of the limited k-range and the high noise level at high k values the two-shell fit is marginally better than the one-shell fit; however, the latter very likely overestimates the Pa-O distance, 2.46 ± 0.02 Å, while the former provides more reasonable distances, Pa-O 2.43 ± 0.02 Å and Pa-Cl 2.70 ± 0.02 Å, in agreement with earlier EXAFS studies on U^{4+} and Np^{4+} in 6 M HCl, U-O 2.43 ± 0.02 Å, U-Cl 2.76 ± 0.02 Å, Np-O 2.42 ± 0.01 Å, and Np-Cl 2.71 ± 0.01 Å.[12-13] The An-O distances in these monochloro complexes are not significantly different from those of the aqua ions in dilute perchloric or hydrochloric acids (Tables S2-S3†).[12-13] Consequently, the Pa-O distance 2.43 ± 0.02 Å is a good estimate for the Pa^{4+} aqua ion.

Fig. 3 plots the mean An-O bond distances of tetravalent actinide aqua ions versus their ionic radii.[17] A linear relationship with a slope of one (0.95) is apparent for the ions from Th^{4+} to Pu^{4+} while the mean Bk-O distance is below this line. No data exist for Am^{4+} and Cm^{4+}, which are both unstable in aqueous solution without complexing anions.[8] Because the An-O bond distance for the ions up to Pu^{4+} follow closely this line, and hence the actinide contraction, we assume that there is no major change in these ions' hydration number, while a decrease in the hydration number, probably from nine to eight, is apparent to occur between Pu^{4+} and Bk^{4+}. Such a change has been debated for the trivalent actinide (and lanthanide) ions, where the ions' hydration number has been reported to either change from nine to eight in the middle of the series or to remain nine across the series up to Cf^{3+}.[18] Further evidence that the regression line in Fig. 3a represent primarily nine-coordinated aqua ions comes from the fact that the mean Th-O bond distance of the Th^{4+} aqua ion is ~0.05 Å shorter than is the ten-coordinate $[Th(H_2O)_{10}]Br_4$ hydrate.[7a]
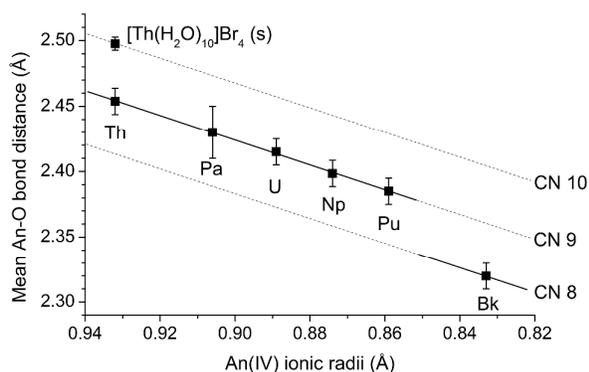
Fig. 3 Mean An-O bond distance vs. An(IV) ionic radii[17] for 8 and 9-coordinated An^{4+} aqua ions from EXAFS data from the present study and from the literature (see Table S3 and references in the ESI†). Note that for Pa^{4+} the stoichiometry is that of $Pa(H_2O)_8Cl^{3+}$, see text. For comparison, single crystal XRD data of $[Th(H_2O)_{10}]Br_4$ is also shown.[7a]

To obtain detailed information on the preferred coordination structure for An^{4+} ions in solution we performed quantum chemical calculations on the decahydrates $[An(H_2O)_{10}]^{4+}$, $[An(H_2O)_9]^{4+} \cdot H_2O$, and $[An(H_2O)_8]^{4+} \cdot (H_2O)_2$; An = Th-Bk (Fig. 4a). The coordination polyhedron of the ten-coordinate isomer with C_2 symmetry is best described as a bicapped square

antiprism, while the nine and eight-coordinate isomers have distorted tricapped trigonal prismatic and square antiprismatic first shell geometries, respectively. The mean An-O bond distance is ~0.047 Å longer for the ten-coordinate isomer than the nine-coordinate one, which is ~0.042 Å longer than the mean bond distance for the eight-coordinated isomer (Fig. 4b, Table S4†). These differences are virtually identical to those between the lines representing ten, nine, and eight-coordinated structures in Fig. 3; however, the absolute An-O distances of the ab-initio structures are slightly larger than the experimental ones.
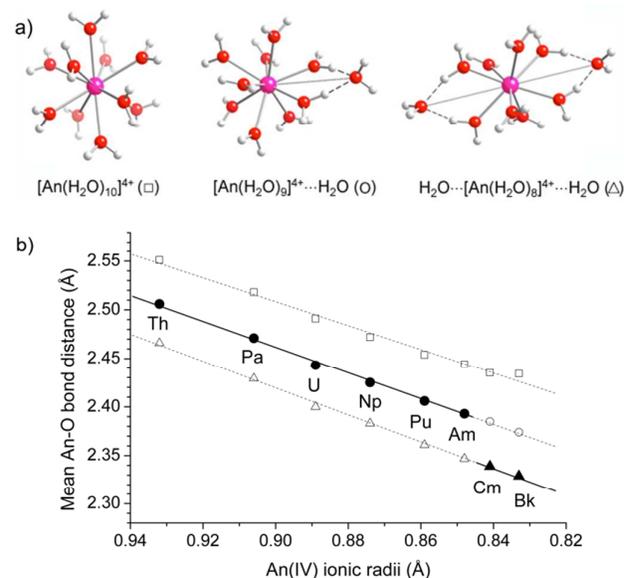
Fig. 4 a) (U)-MP2 gas-phase optimized isomeric 10, 9, and 8-coordinated clusters, $[An(H_2O)_{10}]^{4+}$ (□), $[An(H_2O)_9]^{4+} \cdot H_2O$ (○), and $[An(H_2O)_8]^{4+} \cdot (H_2O)_2$ (△), and b) mean An-O bond distance vs. An(IV) ionic radii[16] of these clusters. Note that filled symbols are used for the data of the most stable clusters (lowest ΔG^{corr} values) while the data for the clusters with lower stability (higher ΔG^{corr} values) are represented with open symbols. Dashed lines are regression lines. For details, see Tables S2-S4 in the ESI†

The relative free energies listed in Table 1 were computed at the best quantum chemical level applicable to molecular systems of this size (density functional theory is not suited for these systems as explained in the ESI†); that is, using the spin-orbit (SO) CASPT2 multi-reference correlated approach in a relativistic framework and modelling bulk solvent effects by a polarizable continuum model, and accounting for an energetic correction for hydrogen bonding between the first and second-hydration spheres.[19] The relative energy between the nine and eight-coordinated ions decreases while that between nine and ten-coordinated ions increases as the nuclear charge increases down the actinide series. This trend is further enhanced when the hydrogen-bond correction to the continuum solvation free energy is applied. Without this correction the relative energies indicate that for all tetravalent actinides the nine-coordinated isomer is energetically the most stable of the three isomers, but when hydrogen bond effects are accounted for the energy

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difference between the nine and eight-coordinated isomers is reduced significantly and an intersection occurs near curium. This *curium break* results in ~5 kJ/mol lower relative energies for the eight-coordinated isomers of Cm^{4+} and Bk^{4+} compared to the nine-coordinated isomers. Thus, all tetravalent actinide ions up to Am^{4+} are predicted by these quantum chemical calculations to be coordinated by nine water molecules in aqueous solution, while for Cm^{4+} and Bk^{4+} the free energy calculation predicts eight-coordination. The short Cm-O (2.34 Å) and Bk-O (2.33 Å) distances of the eight-coordinated quantum chemical clusters $[An(H_2O)_8]^{4+}\cdot(H_2O)_2$ are in line with the bond distance derived from the analysis of the Bk^{4+}(aq) EXAFS spectrum.[7e] In addition, for Th^{4+} the free energy difference between the eight, nine and ten-coordinated ions is relatively large, indicating that the residence time of a first-sphere water molecule is long, in agreement with results from classical and density functional theory-based molecular dynamics simulations.[20]

Table 1. Relative free energies (ΔG), of the $[An(H_2O)_{10}]^{4+}$, $[An(H_2O)_9]^{4+}\cdot H_2O$, and $[An(H_2O)_8]^{4+}\cdot(H_2O)_2$ clusters for An = Th-Bk.[a]

| | $[An(H_2O)_8]^{4+}\cdot(H_2O)_2$ | | $[An(H_2O)_9]^{4+}\cdot H_2O$ | | $[An(H_2O)_{10}]^{4+}$ | |
	ΔG	$ΔG^{corr}$	ΔG	$ΔG^{corr}$	ΔG	$ΔG^{corr}$
Th	25.2	11.3	0.0	0.0	3.7	17.6
Pa	18.4	4.5	0.0	0.0	16.7	30.7
U	16.6	2.7	0.0	0.0	23.9	37.8
Np	17.8	3.9	0.0	0.0	26.0	40.0
Pu	15.1	1.2	0.0	0.0	32.9	46.9
Am	15.0	1.1	0.0	0.0	38.3	52.3
Cm	8.7	-5.3	0.0	0.0	44.1	58.0
Bk	9.4	-4.5	0.0	0.0	44.1	58.0

[a] All values are at the SO-CASPT2 level except for the closed-shell Th(IV) complexes, for which MP2 energies were used; long-range hydration effects were accounted for with the COSMO solvent model, without or with the hydrogen bond correction.

Analysis of the spin density from the multi-reference wave-function for the open-shell systems (Pa^{4+}-Bk^{4+}) reveals a sole occupation of the 5f actinide orbitals, without contributions from the 6d orbitals, regardless of isomer. The nature of the An-O chemical bond has been probed using the topological properties of the electron charge density at the interatomic bond critical point (BCP). At the BCP the density ρ, its Laplacian $\nabla^2\rho$, and the energy density H_b are all in the range usually observed for electrostatic types of bonds (Table S5†); e.g., An^{IV}-N and $U^{VI}O_2^{2+}$-Cl bonds.[21,22] Both ρ and $\nabla^2\rho$ increase along the actinide series. The small increase in ρ from 0.051 to 0.058 e^-/bohr^3 is associated with the slight decrease of the charge on the actinide center. However, the trend we observe is smaller in magnitude than that reported previously for An-O and An-N bonds in An(IV) complexes.[21] These results indicate that the An-O bonds in the series of An^{4+} aqua ions can be described as electrostatic. Also, the electronic and spin density analysis indicate that Pa^{4+} does not distinguish itself from the lighter or heavier An^{4+} ions (Table S6†).

In summary, aqueous Pa(IV) can be stabilized over a period of several days with rongalite, sufficiently long for chemical analysis and characterization. Its fairly long (ns) luminescence lifetime opens a way to TRLFS studies to further elucidate An(IV) speciation in low concentrations ranges, below 10^{-8} M, as expected under environmental conditions. Supported here by EXAFS and quantum chemical methods, the available data for the early tetravalent actinide elements Th^{4+}-Bk^{4+} show that the An-O bonds have a pronounced electrostatic character, with bond distances following the same monotonic decreasing trend as the An^{4+} ionic radii and a decrease of the hydration number from nine to eight for the heaviest ions Cm^{4+} and Bk^{4+}. This is the first sound evidence of a "curium break" in the tetravalent actinide series.

Author Contribution:

All authors have contributed equally to this work. N. L. B, V. V, C. M. M conceived and designed the study; N. L. B, C. M. M performed experimental work; J. R, R. M, M. A. D, the XAFS measurements; C. W TRLFS measurements and V. V, F. R, R. M. B, B. S quantum calculations. The manuscript was written N. L. B, P. L. R, V. V. All authors discussed the results and have given approval to the final version of the manuscript.

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Table of contents synopsis

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