About the existence of Th(III) in aqueous solution

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Abstract—Recently [1] it was claimed that (i) the reaction of $ThCl_4$ with HN_3 in slightly acidic aqueous solution produces the aqueous ion of Th(III) according to the thermodynamically allowed reaction: $Th^{4+} + HN_3 \rightarrow Th^{3+} + 1.5N_2 + H^+$; (ii) Th(III) was identified by its absorption (UV–vis. 200–1300 nm) and ESR spectra. This paper is aimed to prove that the aqueous ion Th^{3+}(aq) is thermodynamically unstable and that the identification of Th(III) in the considered solutions ask for new experiments. © 1998 Elsevier Science Ltd. All rights reserved

Among the chemical properties of the lanthanides, Ln, and actinides, An, the stabilities of aqueous ions in "unusual" oxidation states involving a *d*-electron in the electronic configuration of the ground state of Ln and An is of particular interest [2,3]. The ground electronic configuration of an ion is not always the same in the gaseous state, for instance for Ln and An it could be f^q or $f^{q-1}d$, $f^{q-1}s$ or $f^{q-1}p$ [4,6]. For a gaseous ion, these two configurations are separated by the promotion energy, ΔE. For Th^{3+} gaseous ion, it is known from 50 years ago [4a] that the energies of the configurations $6d^1$ ($^2D_{3/2}$), $7s^1$ ($^2S_{1/2}$) and $7p^1$ ($^2P_{1/2}$) relative to $5f^1$ ($^2F_{5/2}$) are respectively: 1.13856 eV, 2.869 eV and 7.482 eV. Thus for Th^{3+} gaseous ion ΔE, between $5f^1$ and $6d^1$ configurations, is equal to 1.14 eV. This ion belongs to the same category as Np^{2+} ($\Delta E = 0.51$ eV), Pu^{2+} ($\Delta E = 1.61$ eV), Cm^{2+} ($\Delta E = 0.88$ eV) and Pa^{3+} ($\Delta E = 2.07$ eV) [4].

The crystal field effect of ligands, i.e. water molecules, measured by $\Delta(d)$, stabilizes the electronic configurations $6d^1$ by an energy D ($D > 0$, $D > \Delta E$). That is the reason why the old, -3.7 V, [6] recommended redox potential for the pair Th^{4+} (aq)/Th^{3+} (aq) was increased to -3.0 V [5]. It was recently claimed that such potential, -3 V, allows the reduction of Th^{4+} aqueous ion to a Th^{3+} ion, using hydrazoic acid HN_3 [1].

The first part of this paper is devoted to a short analysis of the potentials $E^0(3/2)$ with $f^{q-1}d$ electronic configuration for the reduced specie, to the comparison between $E^0(4/3)$ for Th and Pa and a discussion of the recommended potentials $E^0(4/3)$ for Th given in [5] and [6] in the frame of the crystal field stabilization, D, of a $6d$ electron. In the second part the possibility of the reduction of Th^{4+} ion by HN_3 is considered. Finally, in the last part absorption and ESR spectra, assigned in [1] to a trivalent thorium species, are discussed.

CONSIDERATION ABOUT THORIUM IV/III REDOX POTENTIAL

The stabilization of *d* electrons by crystal field effect was taken into account for the first time in [6] and then in [5], to estimate the redox potentials $E^0(3/2)$ and $E^0(4/3)$ of Ln and An. Unfortunately in [5] the crystal field stabilization was taken twice resulting in an increase of the redox potentials $E^0(3/2)$ (more positive than -3 V) for some dipositive Ln (La^{2+}, Ce^{2+}, Gd^{2+}) and An (Pa^{2+}, U^{2+}, Np^{2+}) ions. Therefore it was emphasized that the ions Ac^{2+}, Th^{2+}, Pa^{2+}, U^{2+}, Np^{2+}, La^{2+}, Ce^{2+} and Gd^{2+} could be stable in aqueous solution.

On the other hand, it was proposed that for the two cations Pa^{3+} (aq) and Th^{3+} (aq) the electronic

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configurations are respectively, fd and f [5]. Regarding the crystal field stabilization effect, D, two limiting cases have to be considered, the weak, $D < \Delta E$, and the strong one, $D > \Delta E$ (Fig. 1). In the former case the electronic configurations f^1 and f^2 should be realized in $Th^{3+}(aq)$ and $Pa^{3+}(aq)$ respectively. The value for the $E^0(4/3)$ (in short for $M^{4+}(aq)/M^{3+}(aq)$) of An with the f^q electron configuration for An^{3+} is given according to [6] by:

$$E^0(4/3)(V) = -4.00 + 1.37\,(q-1) + F_{q-1} \quad (1)$$

From the eqn (1) and with F_{q-1} values from [6] one has: $q = 1$, $F_{q-1} = 0.18$ V and $E^0_{Th}(4/3) = -3.82$ V for Th; $q = 2$, $F_{q-1} = 0.53$ V and $E^0_{Pa}(4/3) = -2.1$ V for Pa if $D(Th^{3+}(aq)) < 1.14$ eV and $D(Pa^{3+}(aq)) < 2.07$ eV, which correspond to the case of a weak crystal field effect.

In order to realize respectively the fd and d electronic configurations in $Pa^{3+}(aq)$ and $Th^{3+}(aq)$ ΔE should be higher than 1.4 eV in the case of $Th^{3+}(aq)$ and higher than 2.07 eV for $Pa^{3+}(aq)$. In this case the eqn (1) is rewritten:

$$E^0(4/3) = -4.00 + 1.37\,(q-1) + F_{q+1} - D - \Delta E$$
$$(2)$$

or

$$E^0_{Th}(4/3) = -4.96 + D \quad (3)$$

$$E^0_{Pa}(4/3) = -4.17 + D \quad (4)$$

For the Ln and An complexes there are no experimental data concerning the crystal field effects $\Delta(d)$ and the stabilization energy D. From calculations for U(IV) complexes with ligands L = F, O, Cl, Br and I in octahedral $(CN = 6)$ and cubic $(CN = 8)$ crystal fields by relativistic Xα SW method, the values of $\Delta(d)$ have been calculated [7]. In the case of cluster complexes $U(IV)O_6^{8-}$, which are the closer to the Th(IV) aqueous ion, the calculated values $\Delta(d)$ are 3.15 and 2.80 eV respectively. The $6d$ electron stabilizations D are 1.26 eV $(CN = 6)$ and 1.68 eV $(CN = 8)$. For a given element the value of D decreases with the decrease of the oxidation state. Thus, in the case U^{3+} (and Th^{3+}) the stabilization energy, D, should be less than 1.3 eV $(CN = 6)$ and 1.70 eV $(CN = 8)$. From spectral data (d-d transitions) for fluoride complexes of $5d$ metals, even in the oxidation states IV–VI, the values of D do not exceed 1.7 eV. Consequently the electronic configuration of $Pa^{3+}(aq)$ is rather f^2 with a small energy gap f^2–fd and $E^0_{Pa}(4/3) = -2.1$ V according to eqn (1). The small excitation energy f^2–fd is one of the reasons of the instability of $Pa^{3+}(aq)$.

The same situation (but with d-f electronic transition or $E(fd) < 0$) occurs for the Th^{3+} species with $D < 1.7$ eV for $Th^{3+}(aq)$ $(CN = 8$–9$)$. The value of $E^0_{Th}(4/3)$ may follow both the eqn (1) or (2) since

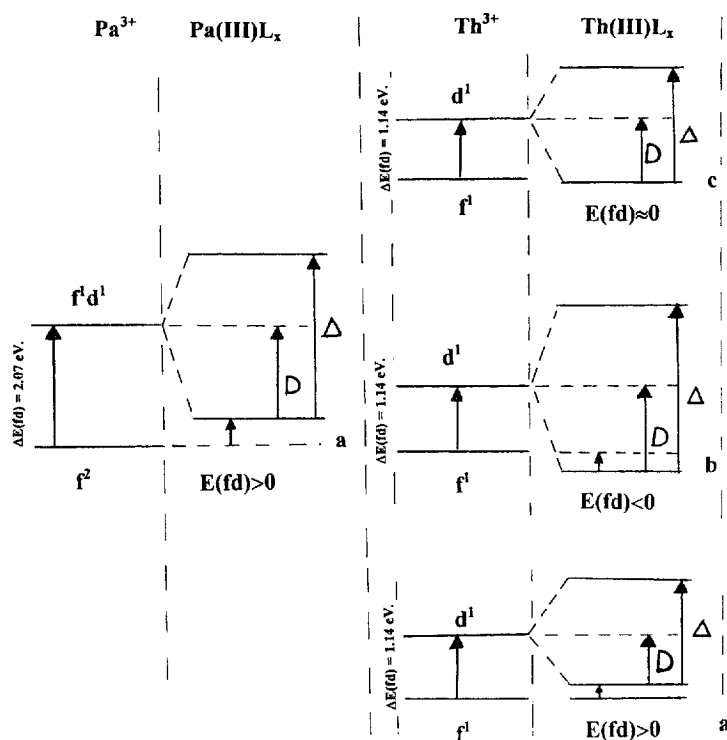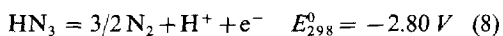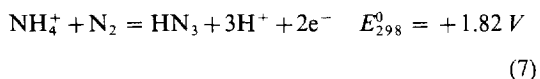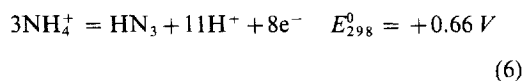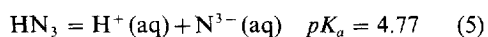Fig. 1. Stabilization of a $6d$ electron of Th^{3+} and Pa^{3+} by crystal field effect; a : $D < \Delta E(fd)$; b : $D > \Delta E(fd)$; c : D around $\Delta E(fd)$.

$\Delta E(\text{Th}) = 1.14$ eV $< \Delta E(\text{Pa}) = 2.07$ eV. The probability that d^1 configuration is the lowest in energy is larger for $\text{Th}^{3+}(\text{aq})$ than for $\text{Pa}^{3+}(\text{aq})$. In [5] and [6] the values of D are 1.96 and 1.26 eV respectively. The first one seems too large and the second one rather small. Thus, with an average value of 1.16 eV (Fig. 1b) and accordingly to the eqn (2) corresponding to a $6d$ lowest configuration, the redox potential $E^0_{\text{Th}}(4/3) = -3.35$ V.

For these reasons the instability of $\text{Th}^{3+}(\text{aq})$ like $\text{Pa}^{3+}(\text{aq})$ ion seems clear. Thus, with a good probability we may accept that $E^0_{\text{Th}}(4/3) = -3.35$ V (d electronic configuration) (Fig. 1b) $> E^0_{\text{Th}}(4/3) > -3.82$ V (f electronic configuration) (Fig. 1a), considering that for $\text{Th}^{3+}(\text{aq})$ a pseudo-degenerated f and d configuration can not be completely ruled out (Fig. 1c).

The reducing ability of HN_3

The dissolution of HN_3 in water gives a weakly acidic solution [9] and its redox behaviour in acidic solutions is quite complex, as the following reactions show:

$$HN_3 = H^+(\text{aq}) + N^{3-}(\text{aq}) \quad pK_a = 4.77 \quad (5)$$

$$3NH_4^+ = HN_3 + 11H^+ + 8e^- \quad E^0_{298} = +0.66 \, V \quad (6)$$

$$NH_4^+ + N_2 = HN_3 + 3H^+ + 2e^- \quad E^0_{298} = +1.82 \, V \quad (7)$$

$$HN_3 = 3/2 \, N_2 + H^+ + e^- \quad E^0_{298} = -2.80 \, V \quad (8)$$

In [1] the value of the redox potential for the reaction (8), $E^0(8)$, used for the discussion was fixed at -3.54 V but not at -2.80 V and for the reaction:

$$\text{Th}^{4+} + HN_3 = \text{Th}^{3+} + 1.5 \, N_2 + H^+ \quad (9)$$
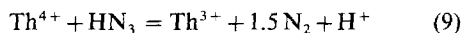
the potential ΔE^0 was estimated as

$$\Delta E^0 = E^0_{\text{Th}}(4/3) - E^0(8) = -3.0 + 3.54 = +0.54 \, V \quad (10)$$

which was the basis to conclude that the reaction (9) is thermodynamically allowed. With the potential $E^0_{\text{Th}}(4/3) = -3.35$ V or -3.82 (and even with -3.0 V) and $E^0(8) = -2.8$ V, ΔE^0 has a negative value, which indicates that, in fact, the reaction (9) is not thermodynamically allowed.

But there are other reasons. The potential $E^0(\text{UO}_2^{2+}/\text{U}^{4+})$ in acid solution is $+0.27$ V [10]. Using the eqns (9) and (10) to forecast the reduction of U(VI) by HN_3, led to the conclusion that this reduction is thermodynamically allowed, but it was established that HN_3 does not reduce U(VI) or U(IV) [21]. The matter is that in acid solution the scheme of potentials for HN_3 follows the step reactions (6) to (8). In analytical chemistry, the reaction of formation

of ferric azide, FeN_3^{2+}, when hydrazoic acid reacts with ferric chloride is used for the qualitative test of the presence of Fe(III) [11]. However the hydrazoic acid does not reduce Fe(III) to Fe(II) although the potential $E^0(3/2)$ for Fe is $+0.77$ V [12]. Finally in neutral solution of thorium salt, the azide anion promotes thorium hydroxide formation and does not form thorium azide:

$$\text{Th}(NO_3)_4 + 4KN_3 + 4H_2O$$
$$= \text{Th}(OH)_4 + 4KNO_3 + 4HN_3 \quad (11)$$
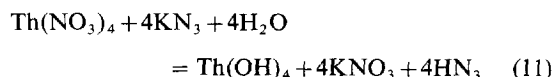
The reaction (11) is used both in qualitative and quantitative determination of Th in the presence of lanthanides. Under the same circumstances, U and Zr are also precipitated as hydroxides [13].

In conclusion there is no firm basis to consider the reaction (9) as thermodynamically allowed.

About the identification of Th^{3+} in HN_3 solutions

In the resultant solutions of the reduction of ThCl_4 with HN_3 the complexes of Th(III), $[\text{Th}(H_2O)_{x-}(N_3)_y\text{Cl}_z]^{3-y-z}$, are supposed to involve N_3, Cl and H_2O ligands. In the tetravalent azido-chloro-complexes of tetravalent Ti, Zr and Hf both terminal, $[(\text{MCl}_4(N_3)_2]^{2-}$, and 1, 1μ-N, $[(\text{M}_2\text{Cl}_8(N_3)_2]^{2-}$, bonding was found for N_3 [14]. If Th(III) or Th(IV) azides exist within the conditions of the considered experiments, the absorption spectra must be explained.

In [1] room temperature optical spectra of proposed Th(III) solution were measured and discussed for a Th concentration of 0.3 mol l^{-1} at pH around 3.5. The quoted concentration is not the result of measurements but is based on the assumption of a 100% yield for the reaction (9) starting with HN_3 2 mol l^{-1} and Th 0.3 mol l^{-1}. The broad band with a maximum at 460 nm = 21.7 kK (which could correspond also to the absorption of ferric azide FeN_3^{2+} [11]), and the peaks at 332 nm = 30.1 kK, 190 mm = 52.6 kK and 185 nm = 54.1 kK were assigned to the $f \Rightarrow d$ and metal $\Rightarrow$ ligand allowed transitions.

Since reaction (9) is not thermodynamically allowed, let us accept for the discussion that the measured spectrum corresponds to an azide complex of Th(IV) involving also chlorine ligands. The linear azide anion belongs to $D_{\alpha h}$ point group. In the $^1\Sigma_g^+$ ground state the 16 valent electrons occupy the 6 MO: $1\sigma_g^2 \, 1\sigma_u^2 \, 2\sigma_g^2 \, 2\sigma_u^2 \, 1\pi_u^4 \, D_{\alpha h}1\pi_g^4$. The highest occupied molecular orbital is the non bonding π_g. Complexes of Th(IV) with ligands having mobile π electron system (most often azo-group) like the azide anion with the non-bonding π electrons have absorption bands within 320–680 nm [15]. For example the dissolution of $\text{Th}(C_9H_6ON)_4$, which is the precipitate of Th by 8-hydroxyquinoline, in 0.1 mol l^{-1} HCl shows absorption at 320–330 nm [15]. In contrast with that on the spectrum reported in [1] at below 650 nm the broad

band until 420 nm (centred at 460 nm) was interpreted as the $f \Rightarrow d$ transition for a trivalent Th complex.

Two kinds of charge transfer bands in the considered complex can be proposed: $N_3^- \Rightarrow Th^{4-}$ and $Cl^- \Rightarrow Th^{4+}$. The intensive absorption at 332, 190 and below 185 nm were interpreted as charge transfer transitions. In fact, the first one (at 332 and 460 nm) could be assigned to $N_3^- \Rightarrow Th^{4+}$ transition and the second and third (at 190 and below 185 nm) could be assigned to the charge transfer $Cl^- \Rightarrow Th^{4+}$.

The equation connecting the charge transfer bands $E(Cl^- \Rightarrow An^{3+})$ and $E(Cl^- \Rightarrow An^{4+})$ for the tetravalent and trivalent actinide chlorine complexes is:

$$E(Cl^- \Rightarrow An^{4+}) = E(Cl^- \Rightarrow An^{3+}) + V_q + \Delta F_q$$

(12)

with $V_q = -33.28$ kK and ΔF_q being evaluated using the approach given in [6]. The correlation between $E(Cl^- \Rightarrow An^{4+})$ and $E(Cl^- \Rightarrow An^{3+})$ can be established (Table 1). For simplicity octahedral complexes MCl_6^{3-} and MCl_6^{2-} are only considered, although the charge transfer energies can be easily recalculated for any symmetry and any CN.

The agreement between the experimental and calculated values $E(Cl^- \Rightarrow An^{4+})$ for An = Pa, U, Np and Pu shows the good validity of eqn (12). It means that values of the charge transfer energies for the considered thorium complexes are satisfactory. The charge transfer energies $E(Cl^- \Rightarrow An^{3+})$ and $E(Cl^- \Rightarrow An^{4+})$ differ approximately on 30 kK. Thus, the intensive absorption "below 185 nm = 54 kK" [1] corresponds to the chlorine-Th(IV) charge transfer (in $ThCl_6^{2-}$ one is at 156 nm = 64.2 kK). In the case of non-octahedral symmetry and higher CN the charge transfer energy would be a little changed. In the part of spectra at about 100 nm (eqn (12) and Table 1) where the charge transfer $Cl^- \Rightarrow Th^{3+}$ is expected, any absorption is measured in [1]. With other hand, the $f \Rightarrow d$ transition in Th(III) complex is waited to be about 1200–1300 nm. These transitions are not observed in [1].

Optical spectra do not confirm firmly the existence

of trivalent thorium but rather those of Th(IV) complexes.

Finally, the ESR spectrum of a frozen solution was given in [1]. The very broad signal is seen very similar in shape to that of UCl_5SOCl_2. The average value of g tensor was measured as $g = 2.19$.

For $[Th(III)\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}]$ the average experimental value of g, $g = 1.91 \pm 0.001$, is interpreted with the assumption of a $6d$ electron configuration [18]. One can see that g values in [1] and [18] differ significantly for a $6d$ electron configuration, which exist in the former case and is assumed in the later. To go further in the discussion let us propose a $5f^1$ configuration for Th, it is to say let assume the existence of Th(III). The g values for the $5f^1$ electron configuration, for example, in UCl_5SOCl_2, UCl_5, $PaCl_5$, $RbUCl_6$ and other compounds is about 1.1 with the sign undetermined (+ or −) [19]. In [20] the value of g for UCl_5SOCl_2 is negative, $g = -1.18$. Thus, it is difficult to understand why the authors of [1] consider an ESR spectrum with $g = 2.19$ as "very similar" to the spectra of UCl_5SOCl_2 with $g = -1.18$.

It seems that the measured ESR spectrum is not connected with Th(III). Without the measurement of the concentration of spins, it is impossible to discuss ESR spectra. Besides, it is known that the decomposition of HN_3 can go through a variety of ways involving the formation of various radicals like nitrogen and imine radical [9,16].

CONCLUSION

In conclusion thermodynamic considerations, room temperature absorption spectra as well as ESR investigations do not support the first observation of Th(III) species in aqueous solution.

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Table 1. Relation between the charge-transfer energy for the tri- and tetravalent actinide chlorine complexes. All data are in kK

An (ΔF_q) [6]	$E(Cl^- \Rightarrow An^{3+})$ [2]	$E(Cl^- \Rightarrow An^{4+})$ calc. [2]	$E(Cl^- \Rightarrow An^{4+})$, exp. [17]
Th (2.825)	94.6	64.2	—
Pa (0.805)	82.9	82.9	50.4
U (−5.08)	77.02	38.7	39.0
Np (−5.566)	71.65	32.8	31.0
Pu (−0.161)	60.86	27.4	27.0
Am (0.483)	49.0	16.2	—
Cm (−26.46)	64.95	5.21	—
Bk (2.03)	51.98	20.7	21.0

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