

COMMUNICATION

The first observation of a Th^{3+} ion in aqueous solution

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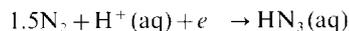
(Received 5 July 1996; accepted 12 July 1996)

Abstract—The reaction of ThCl_4 and HN_3 aqueous solution yielded the Th^{3+} (aq) ion which was identified by its absorption (UV-vis, 200–1300 nm) and ESR spectra. In the high energy region of the electronic spectrum just below 650 nm, a significant and constant signal occurs until 420 nm (maximum at 460 nm), which sees the onset of a very intense, broad band with maxima at ca 332 (shoulder), 190 and below 185 nm. The ESR spectrum of a frozen solution revealed a very broad signal and a main g value of 2.19. Copyright © 1996 Elsevier Science Ltd

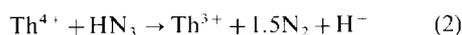
Keywords: thorium chemistry; hydrazoic acid; azides; ESR spectra; electronic spectra.

Recently the electronic structure of f^1 complexes of the early actinide elements ($\text{An} = \text{Pa}, \text{U}, \text{Np}$) has been studied experimentally and theoretically using non-relativistic and relativistic calculations of the optical transition energies of AnX_6^{q-} complexes [1,2]. Examples of actinide f^1 complexes include the tetrahedral borohydride compounds $[\text{Pa}(\text{BH}_4)_4]$ and $[\text{Pa}(\text{BH}_3\text{CH}_3)_4]$ [3], $[\text{Pa}(\eta^8\text{-C}_8\text{H}_8)_2]$ [4] and $[\text{U}(\eta^5\text{-C}_5\text{H}_5)_3\text{NPh}]$ [5], and the isoelectronic octahedral hexahalide complexes $[\text{PaX}_6]^{2-}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$), $[\text{UX}_6]$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) and NpF_6 [6, 7]. Thorium(III) complexes are very rare but intensely coloured organometallic systems such as blue $[\text{Th}(\eta^5\text{-C}_5\text{H}_5)_3(\text{SiMe}_3)_2]_3$ [8], violet $[\text{Th}(\eta^5\text{-C}_5\text{H}_5)_3]$ [9], green $[\text{Th}(\eta^5\text{-C}_5\text{H}_4\text{Me})_3]$ [10] or brown $[\text{Th}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}]$ [9] have been reported. In this communication we report the first observation and identification of a Th^{3+} ion in aqueous solution. As far as we are aware, there are no previous reports on a Th^{3+} ion and it is well-known textbook knowledge that: (i) “the oxidation state III is the only oxidation state which, with the possible exceptions of Th and Pa, is displayed by all actinides” [11a] and (ii) “ Th^{3+} and Pa^{3+} do not exist in aqueous solution” [11b]. (N.B. For organometallic examples compare with refs [8–10].)

We have previously studied the chemistry and bonding of covalent azides and recently extended our studies to hydrazoic acid, HN_3 [12a–c]. The instability of Th^{3+} in aqueous solution can be attributed to the fact that it is rapidly oxidized by air and it reduces water with evolution of H_2 [11a]. The most recent value recommended for the system $\text{Th}^{4+}/\text{Th}^{3+}$ is $E^0 = -3.0$ V [13a] (the earlier recommendation was -3.7 V) [13b]. On the other hand, the reduction potential of HN_3 is more negative than that of any other reducing agent in acidic aqueous solution [Eq. (1)] [11a]. The ΔE^0 value for a reaction according to Eq. (2) can be estimated to $\Delta E^0(2) = +0.54$ V and the reaction is therefore thermodynamically allowed [14]:



$$E^0 = -3.54 \text{ V (pH 3.5, 25}^\circ\text{C)} \quad [15] \quad (1)$$



A solution of Th^{3+} was prepared from aqueous solutions of ThCl_4 and HN_3 [16a]. A solution of ThCl_4 (2.76 g, 7.38 mmol) in 10 cm^3 water ($c = 0.74 \text{ mol l}^{-1}$) was added to 15 cm^3 of a fresh stirred, solution of HN_3 ($c = 2.0 \text{ mol l}^{-1}$) under nitrogen. An amber solution of Th^{3+} was obtained immediately ($c = 0.3 \text{ mol}$

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l^{-1} [16b]; pH ca 3.5 [cf. $pK_a(\text{HN}_3)$ 4.77] [11a]; characterization see below) with evolution of N_2 . The aqueous Th^{3+} solution in hydrazoic acid is stable for more than 1 h before Th^{3+} is slowly oxidized by water to form an insoluble, white, gel-like precipitate of thorium oxide hydroxide [17,18].

Recently, it has been shown that for f^1 complexes most of the $f \rightarrow f$ transitions are orbitally forbidden (N.B. the labels " $f \rightarrow f$ " and " $f \rightarrow d$ " refer to the predominant atomic orbital (AO) character of the molecular orbitals (MOs) involved in the transition) and are therefore observed experimentally as very weak, or are nonexistent [2]. Other transitions are permitted in their own right, and consequently $f \rightarrow d$ and certain charge-transfer bands will have much greater oscillator strengths and will obscure the weaker $f \rightarrow f$ peaks should they occur in the same energy range [2]. Figure 1 shows the higher energy transitions (200–1300 nm) for Th^{3+} [19]. As expected, the spectrum is very similar to the spectrum reported for the f^1 system $[\text{Et}_4\text{N}]_2[\text{PaBr}_6]$ [1] (cf. also ref. [20a,b] and for NpF_6 , ref. [20c]). There are no well-defined $f \rightarrow f$ transitions below 1300 nm. At just below 650 nm, a significant and constant signal occurs until 420 nm (maximum at 460 nm), which sees the onset of a very intense, broad band with maxima at ca 332 (shoulder), 190 and below 185 nm. Since $5f \rightarrow 6d$ and metal \rightarrow ligand charge transfers are allowed transitions, which are usually rather broad and occur in the UV region, the broad band centred at 460 nm as well as the intense absorptions at 332, 190 and below 185 nm can be assigned to such transitions. A number of small shoulders on the main peak occur over the energy range 270–190 nm, but these cannot be justifiably ascribed to well-defined electronic absorptions. Although it is clearly possible that $f \rightarrow f$ transitions occur in this range, there is no means by which they can be assigned with confidence to features in the experimental spectrum (Fig. 1). It should be mentioned, however, that it cannot be completely ruled out that the single electron in Th^{3+}

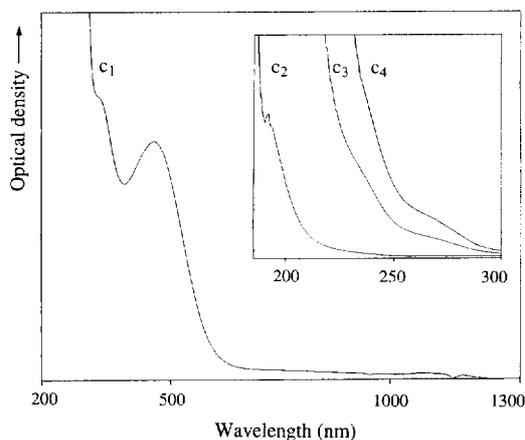


Fig. 1. Room temperature optical spectrum of Th^{3+} in HN_3 solution ($c_1 = 0.3 \text{ mol l}^{-1}$ [16b], $c_2 = 0.01 \text{ mol l}^{-1}$, $c_3 = 5 \times 10^{-3} \text{ mol l}^{-1}$, $c_4 = 2 \times 10^{-4} \text{ mol l}^{-1}$) [21].

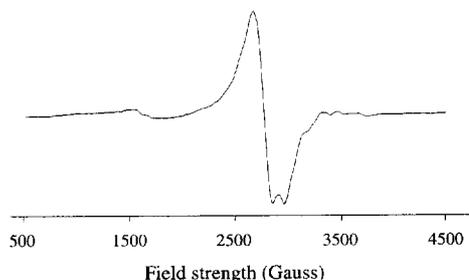


Fig. 2. ESR spectrum of a frozen solution of $[\text{Th}(\text{H}_2\text{O})_x(\text{N}_3)_y(\text{Cl})_z]^{3-}$ ($x+y+z=9$, cf. the CN of La^{3+} in aqueous solution is 9) [11a, 23].

(aq) is a $6d$ rather than a $5f$ electron. In Th^{3+} (g), the $6d$ level lies 9200 cm^{-1} above $5f$, but in the aqueous ion the d orbitals will be stabilized by the ligand field [13b,17]. In this interpretation, the band at 460 nm could be assigned to a $d-d$ transition equal to the ligand field stabilization energy (cf. ref. [1]).

The ESR spectrum of a frozen solution (Fig. 2) shows a very broad signal, very similar in shape to that of the f^1 system $\text{UCl}_5 \cdot \text{SOCl}_2$ [22]. The observed main g value of 2.19 compares with those found for other f^1 systems [6]. The overall shape of the spectrum may well correspond to a system with axial symmetry. However, further experimental and especially theoretical studies have to be carried out to assign the different anisotropic g values with confidence.

Acknowledgements—We thank the University of Glasgow for financial support of this work. We are especially indebted to Dr K. J. Taylor for recording the ESR spectrum.

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14. $\Delta E^0(2) = E^0(\text{Th}^{4+}/\text{Th}^{3+}) - E^0$ [Eq. (1)] = $-3.0 \text{ V} + 3.54 \text{ V} = +0.54 \text{ V}$.
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16. (a) **Safety Note:** Thorium is radioactive and hydrazoic acid is very toxic and, as pure material, explosive [12a]; (b) The quoted concentration of 0.3 mol l^{-1} for Th^{3+} (aq) is not the result of measurement, but is based on the assumption of a 100% yield.
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