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Preparation and Properties of Hydrated Uranium(III) Complex Chlorides. Part I. Uranium Trichloride Heptahydrate

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Abstract

The synthesis of uranium trichloride heptahydrate together with some of its structural, spectroscopic and magnetic properties is reported. The compound possesses the triclinic lattice of $LaCl_3 \cdot 7H_2O$ (space group $P\bar{1}$). Controlled vacuum thermal dehydration of the substance enabled the preparation of the anhydrous trichloride in gram quantities. Magnetic susceptibilities of polycrystalline samples were measured by the Faraday method in the 6.5–295 K range. The uranium trichloride heptahydrate follows in this region the Curie–Weiss law with $C = 1.0839$ emu K mol^{-1} and $\theta = -32.7$ K.

Introduction

The lanthanide trichlorides are known to form two series of hydrates of the types $MCl_3 \cdot 7H_2O$ (M = La, Ce and Pr) and $MCl_3 \cdot 6H_2O$ (M = Sc, Y and Nd–Lu) [1, 2]. In the first series two nine-coordinated Ln ions form a dimer through two bridging chlorines with seven water molecules bound to each of the metal ions (space group $P\bar{1}$). In the second series dimers are not formed and the rare earth ion has a coordination of eight by six water molecules and two chlorines (space group $P2/n$).

As regards the actinides, the preparation of only few hydrates of the trichlorides has been reported [3]. On the basis of ionic size [4], one would expect that if uranium and neptunium form stable hydrates they should contain seven water molecules, whereas all the trichlorides of actinides heavier than Pu should form hexahydrates. Despite the ready oxidation of trivalent uranium in water it has also been shown [5, 6] that uranium in this oxidation state may form stable hydrates.

In a series of papers the synthesis and characterization of new uranium trichloride hydrates and complex hydrates will be presented. This paper reports the preparation of the previously unknown uranium trichloride heptahydrate as well as some of its structural, spectroscopic and magnetic properties.

Experimental

Synthesis

For the preparation of uranium trichloride heptahydrate 3 to 4 g of uranium tetrachloride was dissolved in a solution consisting of 80 ml methyl cyanide, 2.5–3 ml water and 2.5 to 5 ml propionic acid. The solution was well shaken and left standing for at least 12 hours. After filtering the solution was reduced in an inert atmosphere by a 2.4% liquid zinc amalgam in an apparatus described elsewhere [7]. The inert atmosphere may easily be obtained by vacuum evaporation for 2–10 min of the solution and wash liquids. The reduction changed the colour of the UCl_4 solution from olive–green to reddish–brown and resulted in the immediate formation of a fine crystalline, greyish–ink blue precipitate of $UCl_3 \cdot 7H_2O$. A smaller amount of water causes the crystallization of a lower hydrated reddish–brown compound. On the other hand an excess of water or a lower UCl_4 concentration may result in the formation of a separate, oily uranium(III) phase. In this case the crystallization may often be achieved by prolonged cooling at temperatures below −20 °C or for a short time in liquid nitrogen.

The precipitate was thoroughly washed with a degassed 1:40 solution of water and methyl cyanide and finally with freshly distilled ether. The use of anhydrous methyl cyanide causes partial dehydration of the heptahydrate which is manifested by a change in the colour to reddish–brown. The precipitate was next carefully dried under reduced pressure at 20–25 °C and stored in sealed tubes at temperatures below 15 °C. The compound is not stable under prolonged pumping, so drying ought to be carried out with great care.

Reagents

Uranium tetrachloride was prepared from UO_2 by chlorination with CCl_4 vapours according to the procedure given in ref. [8]. Other reagents were of analytical grade.

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Decomposition

The sample of $UCl_3 \cdot 7H_2O$ was decomposed on a MOM type 3427 T derivatograph. The sample, weighing 320 mg, was heated to 500 °C at the rate of 2.5 deg min^{-1} in a pure argon atmosphere flowing at approximately 1000 cm^3 min^{-1}. The loss of 2, 3, 4, 5 and 7 mol of water is clearly indicated in the DTG curve and by weight losses. The decomposition is complete at 260 °C. No further weight loss occurred up to 500 °C.

Analytical Data

Calc. for $UCl_3 \cdot 7H_2O$: U, 50.59; Cl, 22.6; H_2O, 26.8. Found: U, 50.47; Cl, 22.62; H_2O, 27.2. Calc. for UCl_3: U, 69.12; Cl, 30.88. Found: U, 68.9; Cl, 30.31.

Physical Measurements

X-ray powder diffraction data were collected on a DRON-4 diffractometer using Cu-K_α radiation at 23 °C. Unit cell parameters were obtained by a least-squares refinement of 23 values for all observed reflections.

The magnetic susceptibility was measured by the conventional Faraday method on a powdered sample sealed in a quartz tube, at a field of 6 KOe. A variable-temperature liquid helium Dewar was used to enable measurements in the 4–300 K region. The values of the magnetic susceptibilities were corrected for the diamagnetic increment, $\chi_{dia} = -129.0 \times 10^{-6}$ emu mol^{-1}.

In order to obtain the electronic spectra, a mixture of the compound with some Halowax oil* was placed between two quartz windows, approximately 1 cm in diameter, and pressed to get a clear and uniform film. The absorption spectra of such films were recorded on a Cary 14 spectrophotometer in the 4000–21000 cm^{-1} range (Fig. 1).

Results and Discussion

Characterization of the Compound

Uranium trichloride heptahydrate is a crystalline greyish–ink blue solid very soluble in water and the more polar organic solvents. At lower temperatures the compound is relatively resistant to oxidation by air. Above 15 °C the hydrate loses some of its crystallization water and as a result of this then undergoes more or less rapid oxidation.

Carefully controlled vacuum thermal decomposition shows that anhydrous uranium trichloride may be prepared in gram quantities. The method involves the heating of the heptahydrate in a non-static high vacuum system at 25, 60 and 100 °C. The final traces of water can then be removed by increasing the temperature gradually to *ca.* 200 °C. Good results have been obtained with freshly precipitated samples.

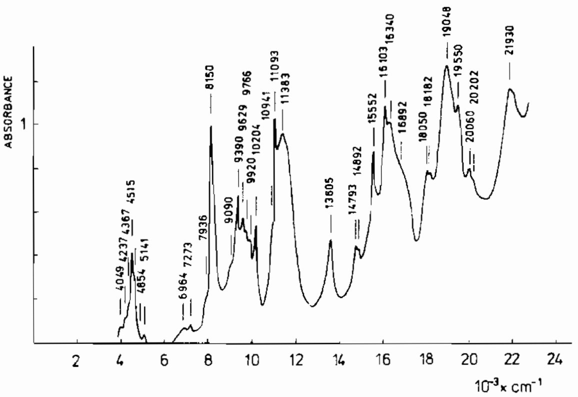
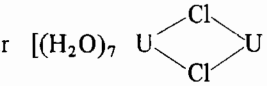


Fig. 1. Absorption spectrum.

When larger amounts are involved it is essential to remove most of the water at lower temperatures to minimize oxychloride formation. The absence of water in the product was confirmed by IR measurements.

X-ray Powder Diffraction Analysis

No qualitative differences were found between the structures of $LaCl_3 \cdot 7H_2O$ [1] and $UCl_3 \cdot 7H_2O$. Hence, one may assume that these substances are isostructural and form similar $[(H_2O)_7$  $\mathrm{U}\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}\mathrm{U}$ $(H_2O)_7]Cl_4$ dimers. The cells are triclinic with space group $P\bar{1}$ and the number of formula units $Z = 2$. From the resolved lines the unit cell dimensions of $UCl_3 \cdot 7H_2O$ were determined with least-squares errors in parentheses: $a = 9.735(3)$ Å, $b = 10.638(3)$ Å, $c = 7.802(3)$ Å, $\alpha = 126.08(1)°$, $\beta = 107.52(2)°$, $\gamma = 90.00(2)°$ and $V = 605.93$ Å^3. The calculated and measured densities are 2.58 and 2.62 g cm^{-3}, respectively. More detailed investigations are in progress [9].

Magnetic Susceptibilities and Electronic Spectra

Uranium trichloride heptahydrate exhibits Curie–Weiss dependence in the whole of the measured region, *i.e.* from 10 to 300 K with the paramagnetic constants $C = (T - \theta)\chi'_M = 1.0839$ emu K mol^{-1} and $\theta = -32.7$ K. This dependence differs from those reported by R. Barnard *et al.* [5] for the hydrated uranium(III) double chlorides where in all cases the plots of the reciprocal susceptibilities against temperature curve below the Curie–Weiss line at temperatures lower than *ca.* 120 K.

The derived magnetic moment $\mu_{eff} = 2.95$ B.M. is much lower than the 'free ion' value which is predicted to lie within the range of 3.70 to 3.79 B.M.

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*Chlorinated naphthalene, refraction index = 1.653.

[10]. Hence, one may hold the crystal field of the water molecules responsible for the low value.

The solid state absorption spectrum of the heptahydrate trichloride is almost identical with that of the aquo ion [11, 12] but exhibits significant differences in comparison with those of the less hydrated uranium trichlorides [9]. These characteristic spectral features are in agreement with the determined structure. A detailed examination of uranium(III) absorption spectra in solution is given elsewhere [13].

Conclusions

The direct vacuum thermal decomposition of the reported uranium trichloride heptahydrate appears to provide a promising alternative method for the preparation of pure anhydrous uranium trichloride, particularly when only gram amounts are required.

The compound appears also to be one of the most suitable starting materials for the preparation of new uranium(III) compounds, especially complex compounds.

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