SOME STUDIES ON THE COORDINATION CHEMISTRY OF URANIUM AND THORIUM

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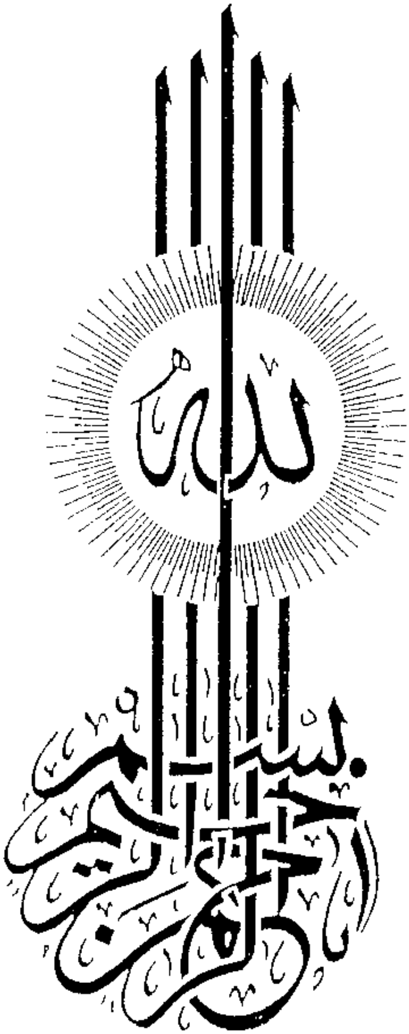
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ABSTRACT

The thesis is divided into two sections.

Section I describes the preparations and properties of some new complex compounds of uranium(VI). The ligands contain atoms from Groups V and VI of the Periodic Table. Uranium(VI) exhibits class "A" acceptor behaviour in which the strength of co-ordination is: N > P, O > S. In most of the uranium(VI) complex compounds water appears to compete in the coordination sphere.

Section II describes the preparations and properties of some new complex compounds of Th(IV). Some physical measurements, elemental analyses, infrared, ultraviolet and visible spectra and TGA measurements were carried out and the results are discussed.

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SECTION I

CHAPTER I

INTRODUCTION

Some Studies on the Coordination Chemistry of Uranium and Thorium

The actinide elements, otherwise known as the 5f transition series, are the fourteen elements which follow actinium, $Z = 89$, in the Periodic Table. They result from the successive addition of electrons to the empty 5f orbitals of the precursor element, and are analogous to the lanthanides, 4f, transition series in this respect. In contrast to the lanthanides, in which the normal oxidation state is +3, both in aqueous solution and in the solid compounds, the actinides exhibit a variety of oxidation states in the early part of the series, up to and including americium[1]. However, the common oxidation state of americium and the remaining elements in aqueous solution is +3, as in the lanthanides, with the sole exception of nobelium, $Z = 102$, for which the dipositive state appears to be extremely stable with respect to oxidation in aqueous solution, apparently a consequence of the filled f shell electron configuration, $5f^{14}$, of the No^{2+} ion.

In the earlier part of the actinide series, the higher oxidation states which can be attained indicate, at least qualitatively, that the fourth and higher ionization potentials for these elements must be much smaller than those for the corresponding part of the lanthanide series. No experimentally determined ionization potential data are available for the actinides, but the differences between the 4f and 5f transition series are probably rather similar to those between the 3d and 4d transition elements.

As we are mainly interested in this work in the coordination chemistry of two of the earlier actinide elements, thorium and uranium, we are going to refer to the chemistry of these two elements and their compounds. The main reasons for this apparent imbalance are simply the availability and the ease of working safely with these two elements and their compounds.

CHEMISTRY OF URANIUM

The first of the actinides to be recognized as a new element was uranium detected in a pitchblende specimen from Saxony by M.H. Klaproth in 1789. The discovery of uranium fission in 1939 by Hahn and Strassman[2] stimulated a detailed study of uranium chemistry, and this led to the discovery of the heavier elements. Uranium is the third element of the actinide series. It is the heaviest element to occur in nature in recoverable amounts. Its isotopes are all α-emitters. Naturally occurring uranium contains three isotopes, 99.28% of ^{238}U, 0.7% of ^{235}U and trace of ^{234}U.[3] Uranium is known to be of great importance because it can be used as a nuclear fuel.

Production of uranium metal usually involves reducing the tetrafluoride with calcium[4] or magnesium[5] or by the reduction of uranium oxide with carbon[6] or by the zinc-magnesium reduction route[7]. The metal can be further purified by the zone melting method[8].

Oxidation States of Uranium

The most stable oxidation state of uranium is uranium(VI). Uranium hexafluoride is technologically important for the separation of the fissible isotope ^{235}U from natural uranium and its physical properties have been extensively investigated[9,10]. Uranium hexafluoride is stable towards nitrogen, chlorine, bromine, carbon dioxide but it reacts violently with water at room temperature; under controlled conditions this reaction yields the hexavalent uranyl-fluoride, UO_2F_2.

Hexavalent Uranyl Compounds:

Uranyl sulphate.- It has been accepted[11] for many years that crystallization of uranium(VI) from aqueous sulphuric acid results in the formation of the yellow trihydrate $UO_2SO_4 \cdot 3H_2O$ for which x-ray and thermodynamic data are available[12]. It is also claimed[13] that thermal decomposition of the trihydrate in air results in the successive formation of a dihydrate, a monohydrate and anhydrous uranyl sulphate; an alternative decomposition[14] involving $UO_2SO_4 \cdot 1.5H_2O$ and UO_2SO_4 has been proposed. The existence of the trihydrate as the stable phase obtained on crystallization from water, and other reports concerning the existence of $UO_2SO_4 \cdot H_2O$[15] and $UO_2SO_4 \cdot 3.5H_2O$[16] have, however, recently been queried by Cordfunke[17] who obtained $UO_2SO_4 \cdot 2.5H_2O$ by drying the initial product of crystallization at 50°C or, alternatively, by allowing anhydrous uranyl sulphate to hydrate over saturated sodium chloride solution. Wet crystals in equilibrium with saturated aqueous uranyl sulphate solutions apparently give the same x-ray powder diffraction pattern as $UO_2SO_4 \cdot 2.5H_2O$, this pattern being somewhat different from that previously reported for $UO_2SO_4 \cdot 3H_2O$. Cordfunke also reported that $UO_2SO_4 \cdot 2.5H_2O$ decomposes directly to UO_2SO_4 without the formation of intermediate hydrates, although it must be recognized that the rate of heating during these experiments, 8°/min, was appreciably faster than the rate 3°/min, employed by certain earlier workers[13]. However, the existence of $UO_2SO_4 \cdot 2H_2O$ as a metastable phase[11] in the UO_2SO_4-H_2O-H_2SO_4 phase system is confirmed by Cordfunke who also reported the formation of $UO_2SO_4 \cdot H_2SO_4 \cdot 2.5H_2O$ at 26°C. It appears that the most satisfactory route to the monohydrate involves heating together stoichiometric amounts of UO_2SO_4 and $UO_2SO_4 \cdot 2.5H_2O$ in a sealed quartz vessel at 200°C for several hours[17]. This compound is unstable when stored at room temperature.

Thermal decomposition of uranyl sulphate hydrates yields the yellow, anhydrous compound above 300°C[18]. No structural data are available for the anhydrous compound. On the basis of Raman studies in non-aqueous solvents the the ν_1 and ν_2 modes of the uranyl group in UO_2SO_4 have been assigned[19]. Absorption and fluorescence spectral data for uranyl sulphate and its hydrates are discussed in the excellent review by Rabinowitch and Bedford[20] and in a more recent publication by Pant and Pande[21]. Thermodynamic data are given[22] where the value calculated for $-\Delta H_{f_{289}}$ is found to be 911 ± 30 Kcal/mole.

According to Lean Marie Leoy *et al*,[23] uranyl sulphate tetrahydrate was prepared by the gentle heating of a solution of 4N H_2SO_4 containing powder UO_3 in stoichiometric proportions. Concentration of the solution to sirupy consistency gave the tetrahydrate, $UO_2SO_4.4H_2O$ after three days. But slow concentration gave another product, $2UO_2SO_4.7H_2O$. The two hydrates gave different sets of compounds on dehydration with only the anhydrous salt in common. It is stated that no passage from one set to the other was possible during dehydration. Each hydrate was characterized by its stability range, its vapour pressure and its x-ray diffraction spectrum.

Solvent extraction experiments of uranyl sulphate indicates that the compound can be extracted[24] from aqueous 1-3M H_2SO_4 solution by shaking with an equal volume of dibutyl hydrogen phosphate or bis(2-ethylhexyl) phosphoric acid in C_6H_6 or CCl_4. Uranium content in the organic phase can either be calculated as the difference, or estimated after re-extraction of uranium with 0.1M sodium carbonate into the aqueous solution.

A series of anhydrous uranyl compounds of the general formula, UO_2XO_4, where X = S, Cr, Mo or W, were studied by L.M. Kovba *et al*[25]. The results obtained reveal that they are all isostructure. Infrared spectra of these compounds confirmed that they can exist as stable anhydrous salts.

Uranyl chloride.- Uranyl chloride is a yellow solid of high melting point, 751°k, which is converted to U_3O_8 on ignition in air. It is moisture sensitive and the monohydrate $UO_2Cl_2 \cdot H_2O$ and a higher hydrate $UO_2Cl_2 \cdot XH_2O$ where $X > 3$, are known. Several methods for the preparation of anhydrous uranyl chloride are reported, probably the best of those[26] is the reaction of uranium tetrachloride with oxygen at 300 to 350°C.

$$UCl_4 + O_2 \xrightarrow{\Delta H} UO_2Cl_2 + Cl_2$$

Mixtures of halides, UCl_6, UCl_5 and UCl_3 also react with oxygen to give uranyl chloride, but UCl_4 appears to be the best starting material and better yields are obtained using this method[26].