THE PREPARATIONS AND PROPERTIES OF SOME COMPLEX COMPOUNDS OF URANYL CHLORIDE, THORIUM CHLORIDE AND NITRATE

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THE PREPARATIONS AND PROPERTIES OF SOME COMPLEX COMPOUNDS OF URANYL CHLORIDE, THORIUM CHLORIDE AND NITRATE

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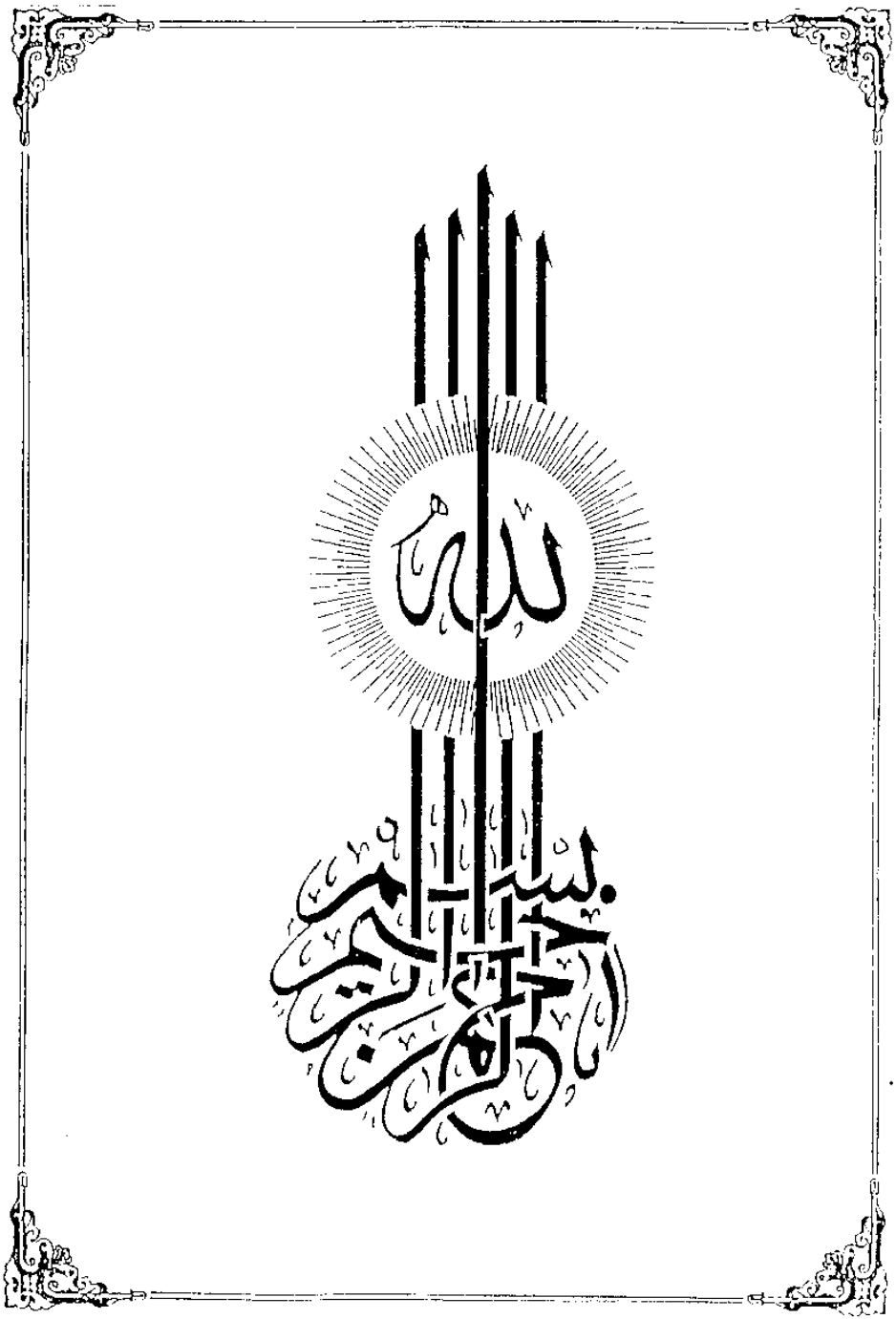

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NOTE

Besides the work carried out in this thesis, the candidate attended post-graduate course for one year in inorganic and physical chemistry covering the following topics:

1. Advanced Inorganic Chemistry.
2. Solvent Extraction.
3. Stability Constant.
4. Nuclear Chemistry.
5. Chemical Kinetics.
6. Advanced Surface Chemistry.
7. Quantum Chemistry.
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ABSTRACT

The thesis is divided into two chapters.

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

Chapter II describes the preparations and properties of some new complex compounds of U(VI). Some physical measurements were carried out and the results are discussed.

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C O N T E N T S

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CHAPTER I

INTRODUCTION

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The Preparations and Properties of

Some Complex Compounds of

Uranyl Chloride, Thorium Chloride

and Nitrate

Historical.- In 1818 Berzelius[1] believed that he had discovered a new earth in a mineral from Fahlun (Sweden) and gave it the name "thoria" after the Scandinavian God Thor. In 1828 Esmark discovered a mineral from Brevig (Norway) from which Berzelius isolated an earth similar to thoria, and the mineral was subsequently called thorite.

In 1898 Madame Curie[2] and Schmidt[3] independently added thorium to the list of naturally occurring radioactive substances.

Occurrence.- The principal thorium minerals[1] are thorite (or thorianite), gadolinite and orangeite, which are silicates of very complex composition; and monazite, which although essentially a cerium Lanthanum phosphate always contains thorium. Monazite sand is the principal commercial source of thorium compounds.

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Electronic Structure.- Methods are described[4] for estimating energies of the electronic configurations of the gaseous ions of the Lanthanides and actinides. Energies are tabulated for the lowest spectroscopic level of the configurations involving 4f, 5d, 6p and 6s electrons for the lanthanide ions and 5f, 6d, 7p and 7s electrons for the actinide ions. Some additional values are listed to be added to the previous tabulation for neutral atoms.

Chemistry of Thorium.- Several books contain sections on the chemistry of thorium and its compounds[3,5,6,7-10]. A comprehensive chemistry of thorium and its compounds, compiled by Pascal[3], covers the literature from 1829 to 1962. A review by Comyns gives a list of complex compounds of thorium(IV) with oxygen and nitrogen donors.

Chemistry of Tetravalent Thorium

Thorium tetrachloride.- Thorium tetrachloride can be made from the elements at a red heat, or by heating the dioxide in a stream of chlorine and sulphur chloride, the $ThCl_4$ being sublimed[11] off

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above 800°C[12-13]. In its purification every trace of air must be excluded, or the oxychloride is formed. It consists of colourless needles fairly stable in air; in a vacuum it begins to sublime at 750°C[14]; the vapour density is normal at 1,000°C, but 24% low at 1,400°C[15]. The electrical conductivity just above the melting point[16] is 0.61-i.e. is that of a fused salt. It dissolves in water with some evolution of heat and considerable hydrolysis; hydrates with 9, 8 and 7 H_2O have been described[17,18].

X-ray studies of thorium tetrachloride showed that thorium is surrounded by eight chlorine atoms in a distorted square antiprism[19]. Four of the chlorine atoms, at 2.46 Å, from a flattened tetrahedron. The other four chlorine atoms are at 3.11 Å. The bonding between thorium and chlorine is on the border between ionic and covalent[20].

Preceding abstract vacuum sublimation of $ThCl_4$ was carried out in order to prepare anhydrous chloride. Properties of the sublimation product and the process conditions were investigated[21]. According to the

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chemical analysis and m.p. measurement, the product was undoubtedly $ThCl_4$, but its X-ray diffraction pattern was quite different from that of the body-centered tetragonal structure formely confirmed as the crystal structure of $ThCl_4$.

Thorium Tetranitrate.- Hydrated thorium tetranitrate can be prepared by dissolving freshly prepared thorium hydroxide in nitric acid. Many hydrates of thorium tetranitrate have been reported with 1, 2, 3, 4, 5, 5.5, 6 and 12 molecules of water of crystallisation.

Density measurements[22] on the commercial sample labelled $Th(NO_3)_4,4H_2O$ suggested that the compound was $Th(NO_3)_4.5H_2O$. Recent X-ray[23] and Neutron diffraction[24] studies showed that in thorium nitrate pentahydrate each thorium atom is surrounded by three water molecules at 2.4–2.5 Å and four bidentate nitrates with oxygen atom at 2.5–2.6 Å. Thus, each thorium has a coordination number of eleven with respect to oxygen. The other two water molecules in the lattice appear to be hydrogen bonded to the nitrate group.

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Lower Oxidation States of Thorium.- There is no evidence for any reduction of Th(IV) in solution. In the solid state[25], the only evidence for lower states is the existence of a black triiodide and of two forms of a golden diiodide[26]. The precise nature of these materials, which are air-sensitive and vigorously attacked by water, is not fully established. The triiodide is believed to contain Th^{3+} ions, but the diiodides may well have the structure $Th^{4+}(I_2^-)(e)_2$ similar to the diiodides of certain lanthanides sulphides such as ThS and Th_2S_3 appear to have Th^{4+} and S^{2-} ions with electrons in conduction bands.

Hydrolysis of Th^{4+}.- Hydrolysis of Th^{4+} in hydrochloric acid is negligible[3] below pH 3 in the concentration range 2.5×10^{-4} M to 1.5×10^{-2} M. Thorium halides are hydrolysed except in strong acid solution, but there is a considerable divergence of opinion about the nature of the hydrolysed species.

Co-ordination Compounds.- Thorium tetrachloride combines vigorously with methyl, ethyl, and isopropyl alcohols to give alcoholates of the general formula

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$ThCl_4$,4ROH. Tertiary pentyl alcohol causes solvolysis and thorium oxychloride is formed[27]. Bradely et al,[28] found that teriary alkoxides can be prepared by alcohol exchange.

$$Th(OPr^i)_4 + 4\ ROH \longrightarrow Th(OR)_4 + 4\ Pr^iOH$$

Sarju Prasad and Suresh Kumar[29] found that amino derivatives of $ThCl_4$ were prepared by addition, with constant agitation, of an Et_2O solution of $ThCl_4$ to dilute Et_2O solutions of various aromatic amines, filtering, washing, and drying the precipitated products. All the compounds were coloured, amorphous, insoluble in Et_2O, CCl_4, $CHCl_3$ and C_6H_6, but sparingly soluble in Me_2CO. The products were stable in dry air and cold H_2O but hydrolysed on long exposure to moist air or when boiled in H_2O or alkali. Compounds may be represented as $[Th.4L]Cl_4$ and $[Th.2D]Cl_4$, where M is a monoamine and D is a diamine.

Th(IV) is known to form high coordination number complexes. An attempt has been made to determine the effect of anions on the coordination complexes of Ph_2SO with Th(IV). The complexes formed were $[Th(Ph_2SO)_6]X_4$

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where X = ClO_4, halogen, NO_3 and NCS groups. In all the complexes Ph_2SO is coordinated to the metal ion through its oxygen. The electric conductances in $PhNO_2$ and in $MeNO_2$ and ebullioscopic molecular weights in MeCN show that the perchlorate and iodide complexes are monomeric and non electrolytes. The ir spectra of the solid complexes indicate the ionic nature of the perchlorate, the bidentate nature of the nitrate and the coordination of thiocyanate through its nitrogen. The perchlorate complex has octahedral symmetry around the Th, the halo- and the thiocyanate complexes are 8-coordinate probably with square antiprismatic structures, while the nitrate complex is 11-coordinate.[30]

Reaction of ThL_4,nH_2O (L^- = Cl^-, Br^-, I^-, NO_3^-, 0.5 SO_4^-, 0.5 $C_2O_4^{--}$) with Me_2SO gave $ThL_4.mMe_2SO,nH_2O$, with m = 1-11 depending on L. The products have νSO of Me_2SO shifted to lower frequencies and it is assumed[31] that these compounds have Me_2SO coordinated to Th^{4+} via oxygen.

Comyns[32] has pointed out the lack of information about nitrate complexes. This is probably because these systems have received little attention rather

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