TOPICS IN INORGANIC
AND GENERAL CHEMISTRY

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P L ROBINSON

MONOGRAPH 15

THE ACTINIDE ELEMENTS

K.W. BAGNALL

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BY

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Preface

The discovery of the first synthetic transuranium elements, *neptunium and plutonium, and the need to develop the production of* the latter for military purposes from 1940 onwards (the Manhattan project) stimulated research on the chemistry of the new elements as well as on the synthesis of elements of atomic number higher than that of plutonium. The latter resulted in the completion of the actinide series in 1961 with the successful synthesis of lawrencium. The interest in research on the chemistry of the actinides grew steadily from 1940, reaching a peak in the middle 1960's. During that time a great deal of the basic chemistry of the members of the group up to americium was reported, and more recently a considerable extension has been made to our knowledge of the elements beyond americium as these have become more readily available, following their large-scale production in the United States of America.

The results of the earlier research, together with the new information on the higher actinides mentioned above, have been used to provide what the writer believes to be a balanced account of the chemistry of the actinides within the covers of a short monograph. In a number of instances the chemical behaviour of the actinides is correlated with that of the lanthanides, showing up similarities and differences between the two series of *f* transition elements. The resulting account is comprehensive, not in the sense of containing every detail, but as a broad survey in some depth which should be useful to those studying or teaching the subject at honours level. This survey has, however, a sufficiently strong backing of references for it to also make accceptable reading to those already engaged in research in this interesting field and may also serve as a helpful point of departure for those planning to undertake new work in the field of actinide chemistry.

Much of the information now presented has not previously been collected together elsewhere. The writer has had to be selective in the choice of the material for presentation in order to restrict the monograph to manageable proportions. To give an instance, complexes of the actinide halides are discussed only by reference to the common stoicheiometries rather than by being given full coverage, for to do this would burden the reader with a considerable mass of almost identical detail. Reviews of this area of actinide chemistry are, however, available and reference is made to them. Other, less well known topics, such as, for example, the alkoxides, carboxylates, chelate complexes and organometallic compounds are treated in considerable detail; in these instances the coverage is as complete as the writer can make it. The monograph closes with a short chapter on *f* orbitals, and the magnetic properties and spectra of the actinides, subjects to which reference has been made in a number of places in the monograph and which are not commonly dealt with at all in the standard textbooks of inorganic chemistry.

I am greatly indebted to Professor P.L. Robinson for critically reading the drafts of the book and for the helpful suggestions which he made at each stage. I am also grateful to a number of my colleagues who have read various parts of the manuscript and suggested the many improvements which have been incorporated into this final version. Finally, I wish to thank the following for permission to reproduce illustrations from their journals; the American Chemical Society, the Chemical Society and the publishers of Acta Chemica Scandinavica, Acta Crystallographica, the Journal of Inorganic and Nuclear Chemistry, Molecular Physics, Nature and Science Progress, as well as the publishers of two books, namely *The Chemistry of the Actinide Elements* by J.J. Katz and G.T. Seaborg and *Man-Made Transuranium Elements* by G.T. Seaborg.

Bramhall, Cheshire, K.W. Bagnall
December 1971

K.W. Bagnall, *The Actinide Elements*, in P.L. Robinson (Ed.), *Topics in Inorganic and General Chemistry*, Monograph 15, Elsevier Publishing Company, Amsterdam, 1972.

ERRATA

page 18, line 4, should read:

> and neodymium, can be oxidised to this higher oxidation state and all of

page 171, 2nd par., line 4, should read:

> about 100°. A uranyl(VI) tellurate of composition
> $UO_2 TeO_4 \cdot 2 Na_2 TeO_4 \cdot 4 H_2O$

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Chapter 1

THE DISCOVERY AND OCCURRENCE OR SYNTHESIS OF THE ACTINIDES

1. INTRODUCTION

The actinide series comprises the fourteen elements following actinium ($Z = 89$) and is analogous to the lanthanide, or rare earth, series in that both result from the filling of the inner $4f$ and $5f$ shells respectively. Although actinium itself is not strictly an actinide element, it is included in the discussion for the sake of comparisons to be made with the chemistry of later elements in the group.

Until 1940, only the first four elements, actinium, thorium, protactinium and uranium, were known; all of them are radioactive, as would be expected from their position at the end of the Periodic Table as it was then known, and it was not until the first of the transuranium elements had been synthesised that the analogy between these elements and the lanthanides was recognised. The classification as a second series of f transition elements was due to G.T. Seaborg, who was personally involved in the discovery and identification of nearly all the transuranium elements.

The filling of the f shell across the lanthanide and actinide groups does not mean that these elements all have the same $nd^1\ (n+1)s^2$ valence configuration; the actual ground state electron configurations of the elements of the two groups are given in Table 1. However, from this it can be seen that, from plutonium onwards, the actinides generally have the same electronic configurations as their lanthanide analogues, whereas the earlier members of the actinide group retain some d electrons in their ground state configurations. Initially in the actinide series the $5f$ level is higher in energy than the $6d$, but as the atomic number increases the energy of the $5f$ level decreases below that of the $6d$ (Fig. 1).

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TABLE 1

ELECTRONIC CONFIGURATIONS OF THE 4f AND 5f ELEMENTS

(Xe core)			*(Rn core)*		
Lanthanum	(La)	$5d6s^2$	Actinium	(Ac)	$6d7s^2$
Cerium	(Ce)	$4f^26s^2$	Thorium	(Th)	$6d^27s^2$
Praseodymium	(Pr)	$4f^36s^2$	Protactinium	(Pa)	$5f^26d7s^2$ or $5f6d^27s^2$
Neodymium	(Nd)	$4f^46s^2$	Uranium	(U)	$5f^36d7s^2$
Promethium	(Pm)	$4f^56s^2$	Neptunium	(Np)	$5f^46d7s^2$ or $5f^57s^2$
Samarium	(Sm)	$4f^66s^2$	Plutonium	(Pu)	$5f^67s^2$
Europium	(Eu)	$4f^76s^2$	Americium	(Am)	$5f^77s^2$
Gadolinium	(Gd)	$4f^75d6s^2$	Curium	(Cm)	$5f^76d7s^2$
Terbium	(Tb)	$4f^96s^2$	Berkelium	(Bk)	$5f^97s^2$ or $5f^86d7s^2$
Dysprosium	(Dy)	$4f^{10}6s^2$	Californium	(Cf)	$5f^{10}7s^2$
Holmium	(Ho)	$4f^{11}6s^2$	Einsteinium	(Es)	$5f^{11}7s^2$
Erbium	(Er)	$4f^{12}6s^2$	Fermium	(Fm)	$5f^{12}7s^2$
Thulium	(Tm)	$4f^{13}6s^2$	Mendelevium	(Md)	$5f^{13}7s^2$
Ytterbium	(Yb)	$4f^{14}6s^2$	Nobelium	(No)	$5f^{14}7s^2$
Lutetium	(Lu)	$4f^{14}5d6s^2$	Lawrencium	(Lw)	$5f^{14}6d7s^2$

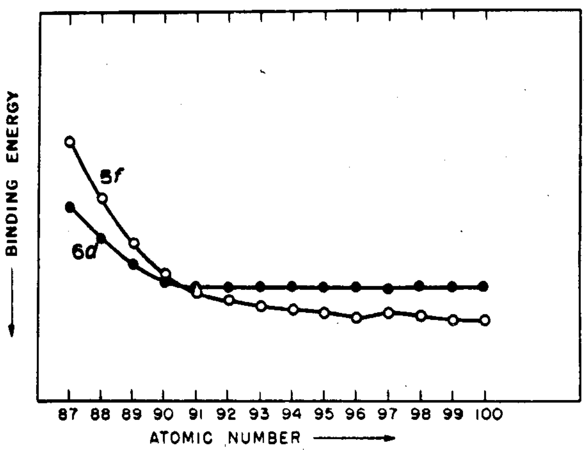

Fig. 1. A qualitative representation of the electronic binding energies in the heaviest elements (J.J. Katz and G.T. Seaborg, *The Chemistry of the Actinide Elements*, Methuen, London, 1957, p. 465. Reproduced by permission of the publishers.

2. THE DISCOVERY OF ELEMENTS 89-92

(a) *Uranium*

Historically uranium is the longest known of all the actinide elements; it was discovered in pitchblende, then thought to be an iron tungstate, by M.H. Klaproth in 1789 and named after Uranus, the planet discovered by Herschel in 1781. Until 1872, when D. Mendeleev assigned uranium to its present position in the Periodic Table, giving it an approximate atomic weight of 240, uranium was thought to have an atomic weight of only 120 which had frustrated earlier attempts to fit it into periodic classifications.

Uranium is by no means rare, occurring[1] to the extent of about 4 ppm in the outermost layer of the earth's crust its abundance being appreciably greater than that of antimony, bismuth, cadmium, iodine, mercury or silver. The principal minerals are oxides, such as uraninite (UO_2), pitchblende ($UO_{2.2}$-$UO_{2.67}$) and uranyl vanadates, such as carnotite [$K_2(UO_2)_2(VO_4)_2 \cdot 1\text{-}3H_2O$] or phosphates, such as autunite [$Ca(UO_2)_2(PO_4)_2 \cdot 8\text{-}12H_2O$], this last being the most common uranium mineral[2].

Towards the end of the nineteenth century, H. Becquerel observed the phenomenon of radioactivity in uranium, thus stimulating research which led to the discovery of a number of other radioelements in this region of the Periodic Table, and, eventually, to the development of the concepts of the nuclear atom and of isotopes. The two principal isotopes present in natural uranium are ^{235}U (0.72 atoms %), which is fissionable by thermal, or slow, neutrons and ^{238}U (99.2%) which is not, and the element became important industrially as a source of nuclear power after the discovery of fission by O. Hahn and F. Strassmann in 1938/39. Before that time almost the only industrial application of uranium was as a colouring material in the manufacture of yellow glass; examples of uranium coloured glass are known which date back to A.D. 79.

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(b) Thorium

Over thirty years after the discovery of uranium, J.J. Berzelius took up again his earlier (1815) work on an oxide which he had named thorine, after the mythological Scandinavian god of war. He had originally thought that the oxide resembled zirconium dioxide, but in 1824 he showed that the parent mineral consisted mainly of yttrium phosphate. In 1828, however, he found that another mineral from Lövö in Norway did indeed contain a new element, chemically analogous to zirconium, to which he gave the name thorium. The mineral is now known as thorite.

Thorium is more abundant than uranium in the earth's crust, the average content being 12 ppm[1], close to that of lead (16 ppm). The principal minerals[2,3] are the silicates thorite and huttonite ($ThSiO_4$) and a hydroxo-silicate variant of thorite, thorogummite, $Th(SiO_4)_{1-x}$-$(OH)_{4x}$, in which tetrahedral groups of four hydroxide ions randomly replace the silicate ions in the lattice. The most important source of thorium is, however, monazite; this is a mixture of lanthanide and thorium phosphates which can contain from 10 to 30% of thorium dioxide.

Following the discovery of the radioactivity of uranium, other heavy elements were investigated and in 1898 Mme. M.S. Curie and G.C. Schmidt independently showed that thorium was also radioactive. Natural thorium is almost entirely ^{232}Th; although this isotope is not fissionable by thermal neutrons it undergoes thermal neutron capture to yield ^{233}U, a fairly long-lived isotope of uranium (1.6×10^5 yr) which does not occur in nature.

$$^{232}_{90}\mathrm{Th}(n,\gamma)\quad ^{233}_{90}\mathrm{Th} \xrightarrow[22.4\ \mathrm{min}]{\beta} {}^{233}_{91}\mathrm{Pa} \xrightarrow[27.0\ \mathrm{days}]{\beta} {}^{233}_{92}\mathrm{U}$$

This isotope of uranium is fissionable by neutrons and suitable as a nuclear reactor fuel. Indeed its formation is important as the basis of the "breeder" reactor, in which escaping thermal neutrons in the outerlying areas of the reactor are captured by thorium instead of being wasted. In this way more nuclear fuel is produced than is consumed in the reactor.

Thorium itself remained industrially unimportant until C.A. von Welsbach's investigations of the emission of light by strongly heated lanthanide oxides (1880–1890), which led ultimately to the discovery that thorium dioxide containing about 1% cerium gave a much greater light emission than any other oxide when heated, a discovery which led to the widespread use of thorium in incandescent gas-mantles. With the decline of gas as a means of illumination, the demand for thorium dioxide decreased; its chief use then was as a refractory material for the manufacture of special crucibles used in high temperature work. Nowadays a principal application is for "breeder" reactors, as mentioned above.

The remaining two naturally occurring elements in this group, actinium and protactinium, have no isotopes of sufficiently long half-life to exist independently in nature, but their longest-lived isotopes, ^{227}Ac (22 yr) and ^{231}Pa (32 500 yr) are both members of the ^{235}U decay chain:

$$^{235}_{92}U \xrightarrow[7.1 \times 10^{8}\ yr]{\alpha} {}^{231}_{90}Th \xrightarrow[25.6\ h]{\beta} {}^{231}_{91}Pa \xrightarrow{\alpha} {}^{227}_{89}Ac$$

(c) *Actinium*

The discovery of actinium is usually attributed to Debierne, who claimed to have isolated it in 1899, but the actual discovery of the element is probably due[8] to Giesel (1900–1902). The name is derived from the Greek ἀκτίς, ἀκτῖνος, a beam or ray, and refers to its radioactivity. Since ^{227}Ac has an extremely short half-life compared with that of ^{235}U, the quantity of the element in equilibrium with one ton of elementary natural uranium is only 0.2 mg and, since the chemical behaviour of actinium is very similar to that of the lanthanides which are generally also present in uranium ores, the separation of the element in a pure state from uranium ores is extremely difficult. There are, however, two alternatives; the parent ^{231}Pa is more easily separable

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