

TOPICS IN INORGANIC
AND GENERAL CHEMISTRY

A COLLECTION OF MONOGRAPHS EDITED BY

P I ROBINSON

MONOGRAPH 15

THE ACTINIDE ELEMENTS

K.W. BAGNALL

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THE ACTINIDE ELEMENTS

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 acceptable 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 stoichiometries 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,
December 1971

K.W. Bagnall

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
 $\text{UO}_2 \cdot \text{TeO}_4 \cdot 2 \text{Na}_2 \text{TeO}_4 \cdot 4 \text{H}_2 \text{O}$

Contents

Preface	V
Chapter 1. <i>The Discovery and Occurrence or Synthesis of the Actinides</i> . . .	1
1. Introduction	1
2. The discovery of elements 89–92	3
(a) Uranium	3
(b) Thorium	4
(c) Actinium	5
(d) Protactinium	6
3. The discovery of elements 93–100	6
4. The discovery of elements 101–103	12
5. Radioactivity and health hazards	14
6. Radioactivity – chemical effects	16
7. References	16
Chapter 2. <i>Oxidation States</i>	18
1. Introduction	18
2. The stability of the +3 oxidation state	22
3. Higher oxidation states in aqueous solution	25
4. References	32
Chapter 3. <i>Separation and Purification</i>	33
1. Introduction	33
2. Thorium	33
3. Uranium	35
4. Actinium	36
5. Protactinium	37
6. Neptunium and plutonium	38
7. Americium and higher actinides	41
8. Analytical chemistry	45
9. References	46
Chapter 4. <i>The Metals</i>	47
1. Introduction	47
2. Physical properties	52
3. Chemical properties	54
4. Preparation of the metals	56
5. References	56

Chapter 5. <i>Compounds with Main Group V Elements</i>	58
1. Introduction	58
2. Preparative methods	58
3. Nitrides	59
4. Phosphides, arsenides, antimonides and bismuthides	61
5. References	63
Chapter 6. <i>Oxides, Hydroxides, Sulphides, Selenides and Tellurides</i>	64
1. Introduction	64
2. Oxides	64
3. Peroxides	69
4. Hydroxides	70
5. Alkali and alkaline earth metallates	71
6. Sulphides, selenides and tellurides	73
7. References	76
Chapter 7. <i>The Halides and Pseudohalides</i>	78
1. Introduction	78
2. The bivalent actinides	79
3. The trivalent actinides	80
(a) Trifluorides	80
(b) Trichlorides	84
(c) Tribromides	88
(d) Triiodides	89
(e) Oxohalides, MOX	90
4. The quadrivalent actinides	90
(a) Tetrafluorides	90
(b) Fluorocomplexes	92
(c) Tetrachlorides	93
(d) Chlorocomplexes	95
(e) Oxygen-donor complexes	96
(f) Sulphur-donor complexes	98
(g) Nitrogen-donor complexes	98
(h) Phosphorus-donor complexes	99
(i) Tetrabromides	99
(j) Bromocomplexes	99
(k) Oxygen-donor complexes	100
(l) Nitrogen-donor complexes	101
(m) Tetraiodides	101
(n) Iodocomplexes	102
(o) Oxygen-donor complexes	102
(p) Nitrogen-donor complexes	103
(q) Oxohalides	103
5. The quinquivalent actinides	105
(a) Pentafluorides	105
(b) Fluorocomplexes	107

(c) Pentachlorides	109
(d) Chlorocomplexes	110
(e) Oxygen-donor complexes	111
(f) Nitrogen-donor complexes	111
(g) Pentabromides	111
(h) Bromocomplexes	112
(i) Oxygen-donor complexes	113
(j) Nitrogen-donor complexes	113
(k) Pentaiodides	113
(l) Iodocomplexes	114
(m) Oxohalides	114
(n) Oxohalocomplexes	119
(o) Oxygen-donor complexes	120
6. The hexivalent actinides	120
(a) Hexafluorides	121
(b) Fluorocomplexes	123
(c) Uranium hexachloride	123
(d) Oxohalides	124
(e) Dioxodifluorides	125
(f) Dioxodichlorides	126
(g) Dioxodibromides	128
(h) Dioxodiiodides	129
7. The pseudohalides	129
(a) Cyanides	130
(b) Thiocyanates	130
(c) Cyanates	132
(d) Selenocyanates	132
8. References	133
Chapter 8. <i>Compounds formed with Inorganic Oxo-acids</i>	141
1. Introduction	141
2. Borates	141
3. Carbonates	142
(a) Actinide(III) compounds	142
(b) Actinide(IV) compounds	142
(c) Actinide(V) compounds	144
(d) Actinide(VI) compounds	144
4. Silicates	146
5. Nitrates	146
(a) Actinide(IV) compounds	146
(b) Actinide(V) compounds	151
(c) Actinide(VI) compounds	153
6. Nitrites	157
7. Phosphates	157
(a) Actinide(III) compounds	157
(b) Actinide(IV) compounds	158

(c) Actinide(V) compounds	160
(d) Actinide(VI) compounds	160
8. Phosphites and hypophosphites	161
9. Arsenates	162
10. Sulphates	163
(a) Actinide(III) compounds	163
(b) Actinide(IV) compounds	164
(c) Actinide(V) compounds	166
(d) Actinide(VI) compounds	166
11. Sulphites	169
(a) Actinide(III) compounds	169
(b) Actinide(IV) compounds	169
(c) Actinide(VI) compounds	169
12. Thiosulphates	170
13. Selenates and selenites	170
14. Tellurates and Tellurites	171
15. Halates	171
(a) Chlorates and bromates	171
(b) Iodates	172
(c) Perchlorates	172
(d) Periodates	175
16. Perxenates	175
17. Compounds of <i>d</i> -transition metal oxoacids	176
18. References	177

Chapter 9. *Carboxylates, Xanthates, Dithiocarbamates, Alkoxides, Phenoxides and Related Sulphur Compounds*

1. Introduction	183
2. Carboxylates	183
(a) Formates	184
(b) Acetates	185
(c) Higher aliphatic acid compounds	188
(d) Oxalates	189
(e) Long-chain dicarboxylates	193
(f) Aromatic carboxylates	193
(g) Ethylenediaminetetraacetic (H_4 EDTA) and nitrilotriacetic (H_3 NTA) acid complexes	194
3. Xanthates, $(ROCS_2)^-$	195
4. Dialkyldithiocarbamates, $(R_2NCS_2)^-$	195
5. Dialkyldiselenocarbamates, $(R_2NCSe_2)^-$	198
6. Alkoxides	198
(a) Tetraalkoxides	199
(b) Pentaalkoxides	200
(c) Hexaalkoxides	202
(d) Uranyl(VI) alkoxides	203
(e) Compounds derived from diols	203

7. Phenoxides	204
8. Mercaptides	205
9. References	205
Chapter 10. Complexes with β-Diketones, Tropolone, 8-Hydroxyquinoline and Other Chelating Ligands	
1. Introduction	210
2. β -Diketone and β -ketoester complexes	210
(a) Actinide(III) complexes	211
(b) Actinide(IV) complexes	214
(c) Actinide(V) complexes	215
(d) Actinide(VI) complexes	216
3. Tropolone complexes	216
4. 8-Hydroxyquinoline complexes	219
(a) Actinide(III) complexes	220
(b) Actinide(IV) complexes	220
(c) Actinide(V) complexes	221
(d) Actinide(VI) complexes	222
5. Cupferron (<i>N</i> -nitroso- <i>N</i> -phenylhydroxylamine) complexes	223
6. Schiff's base complexes	224
7. Phthalocyanine (Pc, tetrabenzoporphyrine) complexes	225
8. References	227
Chapter 11. Borohydrides, Organometallic Compounds and Amides	
1. Introduction	230
2. Borohydrides	230
3. Organometallic compounds	231
(a) π -Allyl complexes	231
(b) Cyclopentadienyl complexes	232
(c) <i>Tris</i> cyclopentadienyl actinides	235
(d) <i>Bis</i> cyclopentadienyl berkelium chloride	238
(e) <i>Tetakis</i> cyclopentadienyl actinides	238
(f) <i>Tris</i> cyclopentadienyl actinide halides	239
(g) <i>Bis</i> cyclopentadienyl uranium dichloride	242
(h) <i>Tris</i> cyclopentadienyl uranium dialkoxides and diphenoxide	242
(i) <i>Bis</i> cyclooctatetraenyl actinides	243
4. Amides and imides	244
5. References	246
Chapter 12. The <i>f</i> Orbitals and the Magnetic Properties and Absorption Spectra of the Actinides	
1. Introduction	249
2. The <i>f</i> orbitals	249
3. Magnetic properties of the actinide ions	253
4. The absorption spectra of actinide ions	256
5. References	262
Subject index	263

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).

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) $5f^{14}6d7s^2$

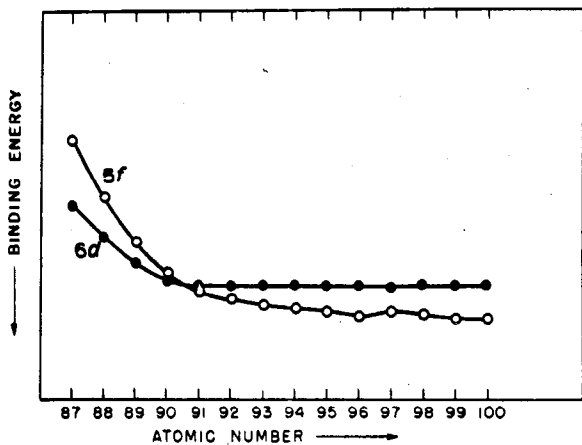


Fig. 1. A qualitative representation of the electronic binding energies in the heaviest elements (J.J. Katz and G.T. Seaborg, *The Chemistry of the Actinide Elements*, Methuen, London, 1957, p. 465. Reproduced by permission of the publishers.

2. ELEMENTS 89-92

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, occurring¹ 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 ($\text{UO}_{2.2}$ - $\text{UO}_{2.67}$) and uranyl vanadates, such as carnotite [$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 1-3\text{H}_2\text{O}$] or phosphates, such as autunite [$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8-12\text{H}_2\text{O}$], this last being the most common uranium mineral².

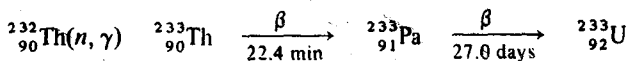
Towards the end of the nineteenth century, H. Becquerel observed the phenomenon of radioactivity in uranium, thus stimulating research which led to the discovery of a number of other radioelements in this region of the Periodic Table, and, eventually, to the development of the concepts of the nuclear 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.

(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 ppm¹, close to that of lead (16 ppm). The principal minerals^{2, 3} are the silicates thorite and huttonite (ThSiO₄) and a hydroxo-silicate variant of thorite, thorumgummit, Th(SiO₄)_{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 ²³²Th; although this isotope is not fissionable by thermal neutrons it undergoes thermal neutron capture to yield ²³³U, a fairly long-lived isotope of uranium (1.6 × 10⁵ yr) which does not occur in nature.

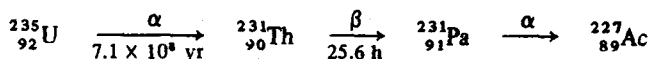


This isotope of uranium is fissionable by neutrons and suitable as a nuclear reactor fuel. Indeed its formation is important as the basis of the "breeder" reactor, in which escaping thermal neutrons in the outlying areas of the reactor are captured by thorium instead of being

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:



(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 due⁸ to Giesel (1900-1902). The name is derived from the Greek *ἄκτις*; *ἄκτινος*, 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

References p. 16