

COORDINATION CHEMISTRY AND PHYSICAL PROPERTIES OF TRANSPLUTONIUM ACTINIDE COMPOUNDS*

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ABSTRACT

Physical properties of the actinide elements which influence their coordination chemistry are discussed and compared with the same properties in other *d* and *f* transition elements. Properties considered include oxidation states, ionic radii, spin-pairing energies, use of *f* orbitals in bonding and ligand field interactions. The coordination properties of the actinide elements are a logical consequence of their position in the periodic system.

I. INTRODUCTION

The coordination chemistry of the actinides was first reviewed in a comprehensive way by Comyns¹ in 1959. Stoichiometries were given for over 500 complexes of the actinides with a variety of organic ligands.

Comyns noted that for each valency state there were close resemblances in coordination behaviour between the various actinide elements, but that the coordination properties of each element were strongly affected by its oxidation state. The trivalent actinides behaved similarly to the trivalent lanthanides.

Comyns concluded that any further systemization of the large amount of data surveyed was largely impossible because of the almost complete lack of structural data.

It is interesting to note that Moeller² and collaborators in an extensive review of the coordination chemistry of the rare earths published in 1965, reported the same lack of structural data for lanthanide complexes.

No essential change in this situation had occurred when Bagnall³ reviewed the coordination chemistry of the actinide halides in 1967. The almost complete absence of precise information on the structures of actinide element complexes with organic donor ligands, noted by Bagnall, persists to the present.

By contrast, those practical aspects of the coordination chemistry of the actinides, related to solvent extraction or ion exchange processes (especially for the technologically important elements thorium, uranium, and plutonium) has received an enormous amount of attention.

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No effort will be made here to deal with this great mass of information. Instead, attention will be directed toward a consideration of such basic properties of the actinide elements as their oxidation states, electronic configurations, use of f orbitals in bonding etc. which determine their co-ordination behaviour.

In this connection it will be helpful to compare the actinides with the lanthanides on one hand and with the d transition elements on the other.

II. OXIDATION STATES AND IONIZATION POTENTIALS OF d AND f TRANSITION ELEMENTS

In general, because of change in electronic configuration, ionic radius, electronegativity etc. associated with a change in oxidation state, the co-ordination behaviour of an element is substantially different in different states of oxidation. Any discussion of the coordination chemistry of an element must, therefore, begin with a consideration of its important oxidation states.

Table 1. Oxidation states of the $4f$, $5f$, $4d$ and $5d$ transition elements observed in their oxides or halides*.

4f		5f		4d ⁺		5d ⁺	
Element	Oxidation states	Element	Oxidation states	Element	Oxidation states	Element	Oxidation states
La	(2)3	Ac	3	Zr	2, 3, 4	Hf	3, 4
Ce	(2)3, 4	Th	3, 4	Nb	2, 3, 4, 5	Ta	2, 3, 4, 5
Pr	(2)3, 4	Pa	3?, 4, 5	Mo	2, 3, 4, 5, 6	W	2, 4, 5, 6
Nd	2, 3	U	3, 4, 5, 6	Te	4, 6, 7	Re	3, 4, 5, 6, 7
Pm	2?, 3	Np	3, 4, 5, 6, 7‡	Ru	3, 4, 5, 6, 8	Os	2, 3, 4, 5, 6, 8
Sm	2, 3	Pu	3, 4, 5, 6, 7‡	Rh	3, 4, 6	Ir	1, 2, 3, 4, 6
Eu	2, 3	Am	(2), 3, 4, 5, 6, 7‡	Pd	2, 3, 4	Pt	1, 2, 3, 4, 6
Gd	(2)3	Cm	3, 4				
Tb	(2)3, 4	Bk	3, 4				
Dy	2, 3	Cf	3, 4				
Ho	(2)3	Es	2?, 3				
Er	(2)3	Fm	2?, 3				
Tm	2, 3	Md	2, 3				
Yb	2, 3	No	2, 3}±				
Lu	3	Lr	3				

* Parentheses indicate state has not been observed in a pure stoichiometric compound

† Data from B. E. Douglas and D. H. McDaniel *Concepts and Models of Inorganic Chemistry*, Blaisdall Publishing Co., New York, 322 (1965)

‡ 1. N. N. Krot and A. D. Gelman, *Dokl. Akad. Nauk SSSR*, **777**, 124 (1967)

2. V. I. Spitsyn, A. D. Gelman, N. N. Krot, M. P. Mefodyeva, F. A. Zakharova, Yu. A. Komkov, V. P. Shilov and I. V. Smirnova, *J. Inorg. Nucl. Chem.* **31** (9), 2733 (1969)

3. V. I. Spitsyn, N. N. Krot, M. P. Mefodyeva and A. D. Gelman, *Dokl. Akad. Nauk SSSR*, **181**, 128 (1968)

Table 1 presents the oxidation states of the $5d$, $4d$, $4f$ and $5f$ transition elements as observed in their halides or oxides. Features of interest exhibited in Table 1 are: (1). The wide range of oxidation states displayed by the light lanthanides, similar to the d transition elements; (2). The dramatic change which occurs in the second half of the actinide series, which exhibits lanthanide-like oxidation-reduction behaviour; (3). The tendency in either d or f transition series for the series with higher principal quantum number

to exhibit higher states of oxidation as compared to the corresponding series of lower n ; (4). The tendency for lower states of oxidation to be relatively more stable in the second half of the transition series of higher n , as compared to the similar series of lower n .

These features may reasonably be interpreted in terms of ionization potentials, exchange interactions between electrons of parallel spin, spin-orbit coupling and interelectronic repulsion. (These phenomena are of course operative for all atomic systems containing more than one electron, and are not confined to the elements of interest here.)

In attempting to understand the resemblances and differences in chemical behaviour exhibited by the $4f$, $5f$, $4d$ and $5d$ elements, it is helpful to consider separately the various factors mentioned above.

Ionization potentials

It is unfortunate that up to the present time not even one accurate measurement of an ionization potential has been possible for any actinide element. Among the lanthanides, first and second ionization potentials are known to ~ 0.2 eV (± 4 kcal) for about half the series. The third ionization potential of lanthanum is known to ± 0.001 eV, and an approximate value has been estimated for praseodymium.

Sums of the first three ionization potentials for the lanthanides have been estimated from Born-Haber cycle calculations by Johnson⁴ while Morss⁵ has performed a similar calculation for plutonium. The data have some reliability in the case of the lanthanides, where the initial calculation may be adjusted to give agreement with the known ionization potentials of lanthanum, but the plutonium value must be regarded as a rough approximation. Relative values for the ionization potentials of $4f$ and $5f$ transition elements must be estimated by indirect methods. In this connection, it is helpful to compare ionization potentials of the $3d$ and $4d$ elements (unfortunately meaningful comparisons cannot be extended to the $5d$ elements because of lack of data). Ionization potentials^{6, 7} for the dipositive gaseous ions of the $3d$ and $4d$ elements indicate that the ionization potentials observed in the $4d$ series are consistently lower than those of the corresponding $3d$ elements by about 79 kcal in the first half of the two series and 55 kcal in the second half.

It is likely that smaller ionization potentials in the $5f$, as compared to the $4f$ elements are important in accounting for the higher oxidation states observed in the actinides, as compared with the lanthanides. Experimental data on this point, however, are not now available.

Electron exchange interactions

Spectroscopists have long been aware of the importance of exchange interactions between electrons of the same spin in lowering the energy of an atomic system. It appears that Jorgensen⁸ was the first to emphasize the importance of this 'spin-pairing energy' in the chemical behaviour of transition elements. The effect amounts to a kind of resonance stabilization proportional to the number of interactions between electrons of the same spin. The number of such interactions is equal to $\frac{1}{2}n(n-1)$ where n is the number of electrons of parallel spin. In a transition series, an added d or f

electron will contribute an additional stabilization proportional to n , where n is the number of electrons already present having spin parallel to the added electrons. The spin-pairing energy is zero for the first electron added beyond the half-filled shell since the Pauli principle demands that the spin of this electron be opposite to the spins of the electrons added previously.

Excitation or ionization of this last electron occurs readily because it entails no loss of spin-pairing energy. The spin-pairing energy increases again as the remaining electrons are added, in the second half of the series. It is now recognized that spin-pairing energy is of dominant importance in understanding the variation with atomic number of the oxidation-reduction behaviour of transition elements. It is particularly important in the f transition elements because the number of exchange interactions rises to a maximum of $\frac{1}{2}(7 \times 6) = 21$, as compared to $\frac{1}{2}(5 \times 4) = 10$ in the d transition elements.

The quantitative importance of the exchange interaction energy will be considered in the subsequent section on Electronic Configurations. Jorgensen^{8,9} has pointed out that the spin-pairing formula needs modification for extra stabilization in the case of atoms or ions having H or I ground terms.

III. ELECTRONIC CONFIGURATIONS OF THE LANTHANIDES AND ACTINIDES

The ground state configurations of the neutral gaseous atoms of the actinide elements have been deduced by a variety of experimental techniques

Table 2. Ground-state electronic configurations of the neutral gaseous atoms of the actinide elements

Element	Ac	Th	Pa	U	Np
Configuration	$6d7s^2$	$6d^27s^2$	$5f^26d7s^2$	$5f^36d7s^2$	$5f^46d7s^2$
Reference	1	2	3	4	5
Element	Pu	Am	Cm	Bk	Cf
Configuration	$5f^67s^2$	$5f^77s^2$	$5f^76d7s^2$	$5f^97s^2$	$5f^{10}7s^2$
Reference	6, 7, 14	8, 13, 14	9, 14	10	11
Element	Es	Fm	Md	No	Lr
Configuration	$(5f^{11}7s^2)^*$	$(5f^{12}7s^2)$	$(5f^{13}7s^2)^*$	$(5f^{14}7s^2)^*$	$(5f^{14}6d7s^2)^*$
Reference	15	12	15	15	15

* As indicated by relativistic Hartree-Fock self consistent field calculations

1. W. F. Meggers, M. Fred, and F. S. Tompkins, *J. Res. Nat. Bur. Stand.* **58**, 297 (1957)
2. P. Schurmans, *Thesis*, Amsterdam (1946)
3. J. Winocur, *Thesis*, University of California, Berkeley (1960)
4. C. C. Kiess, C. J. Humphreys and D. D. Laun, *J. Opt. Soc. Amer.* **36**, 357 (1946).
5. J. J. Katz and G. T. Seaborg, *Chemistry of the Actinide Elements*, p 464. Methuen, London 1957)
6. P. M. Griffin and J. R. McNally, Jr, *J. Opt. Soc. Amer.* **45**, 63 (1955)
7. J. C. Hubbs, R. Marrus, W. A. Nierenberg and J. L. Worcester, *Phys. Rev.* **109**, 390 (1958)
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11. E. F. Worden and J. G. Conway, *J. Opt. Soc. Amer.* **60**, 1144 (1970)
12. L. S. Goodman, H. Diamond, H. E. Stanton and M. S. Fred, unpublished, presented at the American Physical Society Meeting in Seattle, Washington, 23-25 November (1970)
13. R. Marrus, W. A. Nierenberg and J. Winocur, *Phys. Rev.* **120**, 1429 (1960)
14. M. Fred in *Advances in Chemistry Series 71, Lanthanide/Actinide Chemistry*, pp180-202. American Chemical Society, Washington D.C. (1967)
15. Ref. 180 in G. T. Seaborg, *Annual Review of Nuclear Science*, **18**, 53-152 (1968)

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including optical¹⁰⁻¹² and atomic beam resonance¹³⁻¹⁴. The configurations are given in Table 2. It may be noted that 6*d* electrons appear in the ground state configurations of seven of the fifteen actinides and 5*d* electrons appear in the ground-state configurations of five of the fifteen lanthanides.

It is often said that the pronounced difference in chemical behaviour between the lanthanides and the light actinides is due to the similarity in energy between the 5*f* and 6*d* orbitals in the latter. It is of interest, therefore,

Table 3. Energy of the process $f^N d^M \rightarrow f^{N-1} d^{M+1}$ for the neutral gaseous lanthanide and actinide elements*

Element	Ground Configuration	Excited Configuration	Energy (kcal/mol)
La	5 <i>d</i> 6 <i>s</i> ²	4 <i>f</i> 6 <i>s</i> ²	(-92)
Ce	4 <i>f</i> ² 5 <i>d</i> 6 <i>s</i> ²	4 <i>f</i> ² 6 <i>s</i> ²	(-31)
Pr	4 <i>f</i> ² 5 <i>d</i> 6 <i>s</i> ²	4 <i>f</i> ³ 6 <i>s</i> ²	(- 1)
Nd	4 <i>f</i> ⁴ 6 <i>s</i> ²	4 <i>f</i> ³ 5 <i>d</i> 6 <i>s</i> ²	+17
Pm	4 <i>f</i> ⁵ 6 <i>s</i> ²	4 <i>f</i> ⁴ 5 <i>d</i> 6 <i>s</i> ²	(+32)
Sm	4 <i>f</i> ⁶ 6 <i>s</i> ²	4 <i>f</i> ⁵ 5 <i>d</i> 6 <i>s</i> ²	+47
Eu	4 <i>f</i> ⁷ 6 <i>s</i> ²	4 <i>f</i> ⁶ 5 <i>d</i> 6 <i>s</i> ²	+81
Gd	4 <i>f</i> ⁷ 5 <i>d</i> 6 <i>s</i> ²	4 <i>f</i> ⁶ 5 <i>d</i> ² 6 <i>s</i> ²	-27
Tb	4 <i>f</i> ⁹ 6 <i>s</i> ²	4 <i>f</i> ⁸ 5 <i>d</i> 6 <i>s</i> ²	- 3
Dy	4 <i>f</i> ¹⁰ 6 <i>s</i> ²	4 <i>f</i> ⁹ 5 <i>d</i> 6 <i>s</i> ²	(+ 7)
Ho	4 <i>f</i> ¹¹ 6 <i>s</i> ²	4 <i>f</i> ¹⁰ 5 <i>d</i> 6 <i>s</i> ²	(+11)
Er	4 <i>f</i> ¹² 6 <i>s</i> ²	4 <i>f</i> ¹¹ 5 <i>d</i> 6 <i>s</i> ²	+18
Tm	4 <i>f</i> ¹³ 6 <i>s</i> ²	4 <i>f</i> ¹² 5 <i>d</i> 6 <i>s</i> ²	+35
Yb	4 <i>f</i> ¹⁴ 6 <i>s</i> ²	4 <i>f</i> ¹³ 5 <i>d</i> 6 <i>s</i> ²	+70
Lu	4 <i>f</i> ¹⁴ 5 <i>d</i> 6 <i>s</i> ²		
Ac	6 <i>d</i> 7 <i>s</i> ²	5 <i>f</i> 7 <i>s</i> ²	
Th	6 <i>d</i> ² 7 <i>s</i> ²	5 <i>f</i> 6 <i>d</i> 7 <i>s</i> ²	(- 63)
Pa	5 <i>f</i> ² 6 <i>d</i> 7 <i>s</i> ²	5 <i>f</i> 6 <i>d</i> ² 7 <i>s</i> ²	(-31)
U	5 <i>f</i> ³ 6 <i>d</i> 7 <i>s</i> ²	5 <i>f</i> ² 6 <i>d</i> ² 7 <i>s</i> ²	(-14)
Np	5 <i>f</i> ⁴ 6 <i>d</i> 7 <i>s</i> ²	5 <i>f</i> ³ 6 <i>d</i> ² 7 <i>s</i> ²	0
Pu	5 <i>f</i> ⁶ 7 <i>s</i> ²	5 <i>f</i> ⁵ 6 <i>d</i> 7 <i>s</i> ²	+16
Am	5 <i>f</i> ⁷ 7 <i>s</i> ²	5 <i>f</i> ⁶ 6 <i>d</i> 7 <i>s</i> ²	+45
Cm	5 <i>f</i> ⁷ 6 <i>d</i> 7 <i>s</i> ²	5 <i>f</i> ⁶ 6 <i>d</i> ² 7 <i>s</i> ²	0
Bk	5 <i>f</i> ⁹ 7 <i>s</i> ²	5 <i>f</i> ⁸ 6 <i>d</i> 7 <i>s</i> ²	(+23)
Cf	5 <i>f</i> ¹⁰ 7 <i>s</i> ²	5 <i>f</i> ⁹ 6 <i>d</i> 7 <i>s</i> ²	(+29)
Es	(5 <i>f</i> ¹¹ 7 <i>s</i> ²)	(5 <i>f</i> ¹⁰ 6 <i>d</i> 7 <i>s</i> ²)	
Fm	5 <i>f</i> ¹² 7 <i>s</i> ²	5 <i>f</i> ¹¹ 6 <i>d</i> 7 <i>s</i> ²	
Md	(5 <i>f</i> ¹³ 7 <i>s</i> ²)	(5 <i>f</i> ¹² 6 <i>d</i> 7 <i>s</i> ²)	
No	(5 <i>f</i> ¹⁴ 7 <i>s</i> ²)	(5 <i>f</i> ¹³ 6 <i>d</i> 7 <i>s</i> ²)	
Lr	(5 <i>f</i> ¹⁴ 6 <i>d</i> 7 <i>s</i> ²)		

* M. Fred in *Advances in Chemistry Series 71, Lanthanide/Actinide Chemistry*, pp. 180-202. Washington D.C. (1967)

to compare the two transition series with respect to the amount of energy required to change the configuration from $f^N d^M$ to $f^{N-1} d^{M+1}$. These data are presented in Table 3.

The tabulated values show a number of similar *f-d* separation energies between various pairs of elements in the 4*f* and 5*f* transition series: Ce,Pa; Nd,Pu; Sm, Am, etc. Obviously, a similarity in the *f-d* separation energy

for the neutral atoms does not lead to similarity in chemical behaviour of pairs of elements listed above. A more meaningful comparison can be based on the f - d separations observed for the gaseous ions corresponding to the usual states of chemical oxidation.

The limited amount of information available on f - d separations in the gaseous ions is collected in *Table 4*. The data show that the separation of f

Table 4. Configurations and $f \rightarrow d$ transition energies for some gaseous lanthanide ions

Reference	Ion	Transition	Energy (kcal/mole)
a	Th ⁺	$5f7s^2 \rightarrow 6d7s^2$	-10
b	Th ²⁺	$5f6d \rightarrow 6d^2$	-2
b	Th ³⁺	$5f \rightarrow 6d$	+27
c	U ³⁺	$5f^3 \rightarrow 5f^26d$	+76
d	Nd ³⁺	$4f^3 \rightarrow 4f^25d$	+172
e	Gd ³⁺	$4f^7 \rightarrow 4f^65d$	+210
f	Er ³⁺	$4f^{12} \rightarrow 4f^{11}5d$	150

a J. R. McNally Jr, *J. Opt. Soc. Amer.* **35**, 390 (1945)

b P. F. A. Klinkenberg, *Physica*, **16**, 618 (1950)

c J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements*, p. 460, Methuen, Bath (1957)

d D. J. G. Irwin, *Thesis*, Johns Hopkins University (1969), University Microfilms, Ann Arbor, Michigan

e J. F. Kielkopf and H. M. Crosswhite, *J. Opt. Soc. Amer.* **60**, 347 (1970)

f W. J. Carter, *Thesis*, Johns Hopkins University (1966), University Microfilms Inc., Ann Arbor, Michigan, 66-12.510

and d levels increases more rapidly with increase in effective nuclear charge for the $4f$ elements than it does for the $5f$ series. The difference in principal quantum number, therefore, is responsible to a large degree for the decreased availability of $5d$ orbitals in the lanthanides in their common states of oxidation.

In the second half of the actinide series the smaller magnitude of the spin-pairing energy (as compared with the $4f$ elements) produces an interesting alteration in the relative stabilities of the f and d configurations for the elements in the second half of the two series. In the neutral atoms the spin-pairing energy drops by over 100 kcal in passing from Eu to Gd, but only 45 kcal in going from Am to Cm.

Table 5. 'Half-filled shell effects' in p and d transition element gaseous atoms and ions*† (effect in kcal/mole)

Transition series	Neutral atoms	3+ ions	Transition series	2+ ions
$2p$	92	183		
$3p$	50	117	$3d$	134
$4p$	47	113	$4d$	53
$5p$	21	78		

* Atomic Energy Levels, *Circ. U.S. Nat. Bur. Stand. No. 467*, U.S. Government Printing Office, Washington, D.C. (1952)

† B. E. Douglas and D. H. McDaniel, *Concepts and Models of Inorganic Chemistry*, Blaisdell: New York (1965)

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In the second half of the actinide series therefore, the f configuration has gained more than 50 kcal stabilization of $5f$ relative to the alternative $5f^{N-1}6d$ configuration, as compared with the lanthanides.

A similar effect operates with respect to ionization of an f electron. The dipositive state is more stable in the second half of the actinide series than it is in the heavy lanthanide elements. A decrease in spin-pairing energy with increase in principal quantum number is observed throughout the periodic system. 'Half-filled shell effects' for p and d gaseous ions are given in *Table 5*. The data presented in *Tables 5* and *6* indicate that in general the spin-pairing

Table 6. Increase in ionization potential per d electron added in $3d$ and $4d$ transition series. Dipositive gaseous ions*†

Initial No. of d electrons	Δ in eV $3d$	Δ in eV $4d$
1	3.4	4.3
2	3.6	3.3
3	1.2	- 1
4	2.7	2.3
5	-3	-1.1
6	2.8	3.6
7	2.7	1.9
8	0.73	1.9
9	2.7	2.6

* Atomic Energy Levels, *Circ. U.S. Nat. Bur. Stand. No. 467*, U.S. Government Printing Office, Washington, D.C. (1952)

† B. E. Douglas and D. H. McDaniel, *Concepts and Models of Inorganic Chemistry*, Blaisdell: New York (1965)

energy in a given type of transition series will always decrease with increase in principal quantum number of the shell being filled, as is observed in the $4f$ and $5f$ series.

IV. IONIC RADII, IONIC POTENTIALS AND ELECTRONEGATIVITIES OF THE ACTINIDE ELEMENTS

Although an 'ionic radius' cannot be defined exactly, and the concept should be used with care, numbers may be assigned to the elements in specified states of oxidation that are useful in predicting interatomic distances in crystals and rationalizing their coordination behaviour.

A widely accepted set of radii for the trivalent lanthanides based on measured interatomic distances in the cubic sesquioxides, has been published by Templeton and Dauben¹⁷. Lattice parameters have been measured for a number of actinide sesquioxides, from which ionic radii may be derived by the same process that has been applied to the rare earths. For thorium and protactinium the sesquioxide does not exist, and for actinium, californium and einsteinium the lattice parameters of the trichlorides are known more accurately at present than the parameters of the sesquioxides. In the latter

cases it is possible to convert the trichloride data to 'sesquioxide ionic radii', in a consistent way⁵.

The radii of the tetrapositive ions have been determined from the lattice parameters of the fluorite-type dioxides, using 1.38 Å for the radius of ${}^{IV}\text{O}^{2-}$, with a cation coordination of four, and an appropriate correction to coordination number *vi* for the cation, as recommended by Shannon and Prewitt¹⁸.

The radii, reported here for the +2, +5 and +6 oxidation states are those given by Zachariassen¹⁹.

Ionic radii for the lanthanide and actinide elements in various states of oxidation are given in *Tables 7, 8 and 9*. Both the lanthanide and actinide

Table 7. 'Cubic sesquioxide ionic radii' for the lanthanides and actinides*†

Element	Ac	Th	Pa	U	Np	Pu	Am	
Radius (Å)	1.17‡	—	—	1.03‡	1.02‡	0.99	0.98	
Element	La	Ce	Pr	Nd	Pm	Sm	Eu	
Radius (Å)	1.06	1.03	1.01	0.99	0.98	0.96	0.95	
Element	Cm	Bk	Cf	Es	Fm	Md	Mo	Lr
Radius (Å)	0.98	0.95	0.95	0.94	(0.93)§	(0.92)§	(0.91)§	(0.90)§
Element	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Radius (Å)	0.94	0.92	0.91	0.89	0.88	0.87	0.86	0.85

* Lanthanide radii from D. Templeton and C. H. Dauben, *J. Am. Chem. Soc.* **76**, 5237 (1954)

† Actinide radii from L. Morss, *Thesis*, University of California Lawrence Radiation Laboratory Report UCRL-18951, Berkeley (1969)

‡ Calculated from trichloride data

§ Extrapolated value

Table 8. 'Dioxide ionic radii' for the lanthanides and actinides*

Element	Ac	Th	Pa	U	Np	Pu	Am	
Radius (Å)	—	0.96	0.92	0.91	0.89	0.88	0.87	
Element	La	Ce	Pr	Nd	Pm	Sm	Eu	
Radius (Å)	—	0.88	0.88	—	—	—	—	
Element	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Radius (Å)	0.87	0.85	—	—	—	—	—	—
Element	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Radius (Å)	—	0.80	—	—	—	—	—	—

* L. R. Morss, *Thesis*, University of California Lawrence Radiation Laboratory Report UCRL-18951, Berkeley (1969)

Table 9. Approximate ionic radii for +2, +5, and +6 states of the lanthanides and actinides †

Element and oxidation states	Sm(II)	Eu(II)	Yb(II)	Es(II)	Pu(V)	Pu(VI)
Radius (Å)	1.11	1.09	0.93	(1.01)*	0.87	0.81

* Estimated

† W. H. Zachariassen in *National Nuclear Energy Series Division IV Plutonium Project Record* Vol. 14A pp. 775-776; (edited by G. T. Seaborg and J. J. Katz), McGraw-Hill: New York (1954)

radii show the familiar 'cusp' at the half-filled shell, i.e. at gadolinium 3+ and curium 3+. The variations in the radii as a function of atomic number are of considerable interest, as they are often compared with variation in the stabilities of complexes, ion exchange separation factors, etc.

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If the cusp represents a half-filled shell effect, as appears reasonable, it should occur one element later (i.e. at berkelium) for the +4 actinides. Unfortunately, the +4 radius of californium is not accurately known at present. For the +2, +5 and +6 states of the lanthanide or actinide elements 'ionic radii' are less well defined than for the +3 and +4 states; the +2 radii are uncertain because of lack of precise knowledge of the stoichiometry of pertinent compounds and the +5 and +6 'ionic radii' because the nature of the bonding is in these states uncertain. Approximate values for these states are presented, however, in *Table 9*.

The tabulated radii may be used to calculate ionic potentials, which sometimes are of use in comparing the strengths of ionic complexes formed by different elements. Some values for the ionic potentials of the lanthanides and actinides are given in *Table 10*. It will be noted that the lanthanide and actinide elements exhibit low ionic potentials compared with other elements of

Table 10. Ionic potentials of various mutual ions

Ion	Sm ²⁺	Yb ²⁺	Es ²⁺	Gd ³⁺	Cm ³⁺	Ce ⁴⁺	Pu ⁴⁺
Ionic potential	1.97	2.14	1.98	3.2	3.1	4.5	4.5
Ion	Pu ⁵⁺	Pu ⁶⁺	Fe ²⁺	Fe ³⁺	Al ³⁺	Nb ⁵⁺	Mo ⁶⁺
Ionic potential	5.7	7.3	2.6	5.7	6.0	7.1	9.7

the same oxidation state, and on this basis their ionic complexes would be expected to be correspondingly less stable.

Finally, we may consider another property of the lanthanides and actinides related to their electron attracting (and hence complexing) ability: namely their electronegativities. Using available thermodynamic data Allred²⁰ in 1961 calculated the electronegativities of uranium, neptunium and plutonium. For these elements he found values of 1.4, 1.4 and 1.3 on the Pauling scale. Corresponding values for the lanthanides are 1.1 to 1.3 for the sequence from the lanthanum to lutetium. The actinides are thus similar in electronegativity to the rare earth elements.

V. PARTICIPATION OF *f* ORBITALS IN BONDING

Much of the coordination chemistry of the *d* transition elements is governed by the participation of *d* orbitals in bonding, and the energetics of such complexing has been interpreted in terms of crystal or ligand field interactions.

The possible participation of *f* orbitals in bonding was considered by Kimball²¹ in 1940 and Hugas²² in 1952 proposed that the enhanced stability of the higher oxidation states of antimony, tellurium and iodine, as compared with arsenic, selenium and bromine, was associated with the use of *f* orbitals in bonding. However, most attention has been given to the possible utilization of *f* orbitals in bonding in the actinides. The radial extension of 4*f* and 5*f* orbitals as a function of atomic number was considered by Mayer²³ as early as 1941 and led, of course, to the prediction of a new *f* transition series beginning in the neighbourhood of atomic number 90. Because of the greater

radial extension of the $5f$ as compared with the $4f$ orbitals, greater participation of the former in bonding was to be anticipated.

The formation of σ bonds by hybridization of f with s , p and d orbitals was considered by Dyatkina²⁴ about twenty five years ago. Experimental evidence for the use of f orbitals in bonding was claimed by Connick and Hugas²⁵ on the basis of the difference in chemical behaviour between the known +5 actinides on the one hand, and niobium, tantalum and protactinium on the other. These authors argued further that the persistence of the linear $O-M-O^{2+}$ grouping (with short metal-oxygen distances) in solutions and solids was unique to the actinides and indicated the use of $5f$ orbitals in the metal-oxygen bond.

The grouping of six equivalent oxygens in a planar or puckered arrangement in the equatorial plane perpendicular to the linear UO_2^{2+} grouping, [observed in such compounds as $RbUO_2(NO_3)_3$] suggested the participation of $5f$ electrons in bond formation and thermochemical evidence for the strong bonding of water of hydration in $UO_2(NO_3)_x$ ($x = 2$ or 3) as compared to the binding by Ba^{2+} , was considered by Kapustinskii and Baranova²⁶ to represent a quantitative difference in the bonding in the two cases. A consideration of the paramagnetic resonance spectrum of $RbNpO_2(NO_3)_3$ by Bleaney *et al.*²⁷ provided strong evidence for the overlap of f electrons with neighbouring atoms in this compound. Eisenstein²⁸ calculated the relative strengths of various hybrid bonds involving f orbitals and concluded that dative covalent σ bonds were formed between U and O in UO_2^{2+} from linear df hybrids. Pi bonding occurred additionally by overlap with the $2p$ orbitals of oxygen. Other hybrid orbitals suggested by Eisenstein were d^2sf^2 (octahedral complexes), sf^3 (tetrahedral) and sf^2d (square). Coulson and Lester²⁹ considered the use of f orbitals in the formation of hybrid bonds in UO_2^{2+} and similar complexes and concluded that use of $6f$, rather than $5f$, orbitals was energetically more favourable.

More recently, Kettle and Smith³⁰ have considered carefully the stereochemical consequences of f orbital participation in metal-ligand bonding. They present the irreducible representations spanned by f orbitals in all common point group symmetries, and list molecular geometries indicative of f orbital participation. They also give i.r. and Raman-active modes for metal-ligand stretching frequencies and suggest that such spectroscopic information will be useful in recognizing f orbital bonding participation, in the absence of precise structural data. A number of actinide compounds whose structures are considered to suggest the utilization of f orbitals in bonding were listed by Kettle and Smith³⁰. These authors conclude, however, that definite evidence from crystallographic data or the use of f orbitals in bonding is lacking.

Direct evidence for a greater spatial extension of $5f$ as compared with $4f$ orbitals, and of overlap of the former with adjacent atoms was provided by Bleaney *et al.*³¹⁻³³ in their observation of super hyperfine interaction between uranium 3+ and F^- in CaF_2 or SrF_2 containing small amounts of uranium; whereas no super hyperfine interaction was observed for neodymium 3+ in the same host.

Since it had been shown in other experiments^{32, 33} that both uranium 3+ and neodymium 3+ exhibited a $^4I_{9/2}$ ground term, the observed additional

interactions in the case of uranium 3+ could only be interpreted in terms of overlap of the $5f$ wavefunction with neighbouring F^- ions. Quite recently, super hyperfine lines due to the interaction of plutonium 3+ in CaF_2 with the surrounding F^- ions have been observed by Edelstein *et al.*¹⁵.

Great interest was aroused about two years ago by the announcement of Streitweiser and Mueller-Westerhoff³⁴ of the discovery of a new type of sandwich compound: bis(cyclooctatetraenyl)uranium (uranocene)—similar to the cyclopentadiene compounds. A determination of the structure of uranocene by Zalkin and Raymond³⁵ showed that in this compound the uranium atom lies between two parallel planar cyclooctatetraene rings in the eclipsed position ($D8h$) with all U—C bond lengths equivalent. The bonding involves the use of $5f_{z^3}$, $5f_{xz^2}$, $5f_{yz^2}$, f_{xyz} and $f_{z(x^2-y^2)}$ orbitals³⁴. Isostructural compounds of plutonium(IV) and neptunium(IV) have been prepared also, and investigated by p.m.r. and Mössbauer spectroscopy¹⁶. The Mössbauer spectrum of $Np(COT)_2$ shows a larger isomer shift relative to neptunium 4+ in ionic compounds, indicating a large shielding of the nucleus by electron density from the $6s$ shell. This is direct evidence for covalent bonding in this compound.

In summary it can be said that strong evidence for the participation of orbitals in bonding in the actinide elements now exists for the III, IV and VI oxidation states. It is interesting to note that Axe and Burns³⁶ have suggested an appreciable amount of covalent character in the bonding between thulium²⁺ and F^- in CaF_2 and SrF_2 crystals doped with thulium.

VI. CRYSTAL FIELD EFFECTS

Crystal (ligand) field effects in the lanthanides have been studied by magnetic, thermodynamic and optical methods for over 35 years³⁷⁻³⁹. Typical overall splittings of the ground term are about 150 cm^{-1} ⁴⁰. Crystal field splittings in the tripositive actinides have been observed by Edelstein *et al.*¹⁵ for Pu^{3+} in cubic symmetry sites in CaF_2 and by Lammerman and Conway⁴¹ for Pu^{3+} in $LaCl_3$.

In CaF_2 the total splitting was observed to be about 300 cm^{-1} . Typically, crystal field splittings in the tripositive actinides are two to three times as large as those observed in the lanthanides⁴². For Np^{4+} in $PbMoO_4$ Sharma and Ortman⁴³ observed a splitting of about 700 cm^{-1} , while Gruen, Malm and Weinstock⁴⁴ conclude that in PuF_6 the ligand field splitting must exceed 1000 cm^{-1} . Thus in the tri- and tetra-positive lanthanides and actinides crystal field splittings are at most about ten per cent of those of the smallest splittings observed in d transition elements. Crystal field stabilization energies are correspondingly smaller and the effects, consequently, more difficult to detect.

For the hexapositive (and probably the pentapositive) states, the ligand field effects should be large enough to detect by thermodynamic measurements. Unfortunately, little accurate thermodynamic data exist for the +5 and +6 compounds. In spite of the small ligand field splittings of the lower oxidation states of the actinide elements, careful measurements of Kds or equilibrium constants could be expected to reveal their existence. For example, a difference of only ten per cent in distribution coefficients is

readily detectable by ion exchange methods. This difference corresponds to only 53 calories (18 cm^{-1}) of energy at room temperature. Of course, crystal field splittings may be more readily detected by paramagnetic resonance techniques or very low temperature magnetic susceptibility measurements.

In summary, crystal field or ligand field splittings in the tri- or tetra-positive actinides, although larger than in the rare earths, are of relatively slight thermodynamic significance, unlike the situation that prevails in the *d* transition elements. They may be of considerable importance in the 5 and 6 states, however.

VII. COORDINATION IN LANTHANIDE AND ACTINIDE OXIDES, FLUORIDES, CHLORIDES AND AQUO IONS

It is of interest to consider the coordination behaviour of the lanthanide and actinide ions first on the basis of simple close packing considerations. The radii for the *4f* and *5f* elements in different states of oxidation have been given. From these radii and assumed radii of 1.38, 1.33 and 1.81 Å for O^{2-} , F^- and Cl^- , respectively, calculated radius ratios are obtained as given in Table 11. The calculated radius ratios suggest an unexpected coordination

Table 11. Calculated radius ratios, R_M/R_X , for lanthanide and actinide oxides, fluorides and chlorides

M	$\frac{R_M}{R_{\text{O}^{2-}}}$	$\frac{R_M}{R_{\text{F}^-}}$	$\frac{R_M}{R_{\text{Cl}^-}}$
$\text{Eu}^{2+} \rightarrow \text{Yb}^{2+}$	0.81 → 0.68	0.82 → 0.70	0.61 → 0.51
$\text{Es}^{2+} \rightarrow \text{No}^{2+}$	0.73 → 0.71	0.76 → 0.74	0.56 → 0.54
$\text{La}^{3+} \rightarrow \text{Lu}^{3+}$	1.06 → 0.85	0.80 → 0.64	0.59 → 0.47
$\text{Ac}^{3+} \rightarrow \text{Lr}^{3+}$	1.17 → 0.90	0.88 → 0.68	0.64 → 0.50
$\text{Ce}^{4+} \rightarrow \text{Tb}^{4+}$	0.64 → 0.58	0.66 → 0.60	0.49 → 0.44
$\text{Th}^{4+} \rightarrow \text{Bk}^{4+}$	0.70 → 0.62	0.72 → 0.64	0.53 → 0.47
U^{5+}	0.63	0.65	0.48
U^{6+}	0.59	0.61	0.45

number of eight for the lanthanide and actinide monoxides, sesquioxides, most difluorides and a considerable number of trifluorides. In the remaining compounds 'hard-sphere' radius-ratio considerations suggest a coordination

Table 12. Electronegativities of some actinide and other elements*

Element	Pt	U	Np	Pu	La	Lu				
Electronegativity	2.2	1.4	1.4	1.3	1.1	1.3				
Element	C	Sc	N	P	O	S	F	Cl	Br	I
Electronegativity	2.6	1.9	3.0	2.2	3.4	2.6	4.0	3.2	3.0	2.7

* A. L. Allred, *J. Inorg. Nucl. Chem.* 17, 215 (1961)

number of six. It is of interest to compare these expectations with coordination numbers actually observed in the actinide and lanthanide oxides, fluorides and chlorides.

Aquo ions

One of the most important aspects of the coordination behaviour of an element in aqueous solution is its coordination behaviour towards water. Coordination of the aquo ions of the lanthanides and actinides remains uncertain to a degree, although some important observations have been made. Among the earliest were those of Helmholtz⁴⁵, whose investigations of the structure of $\text{NdBr}_3 \cdot 9\text{H}_2\text{O}$ indicated that nine water molecules were bonded to the neodymium cation; of Marezio, Plettinger and Zachariasen⁴⁶, who showed that six water molecules and two chlorides were bound to the central Gd^{3+} cation in $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$; and of Morgan⁴⁷, who concluded from proton relaxation measurements in $\text{Gd}(\text{ClO}_4)_3$ solutions that eight or nine water molecules were bound to the Gd^{3+} ion in the central coordination sphere.

Studies by Miller⁴⁸ on the absorption spectrum of $\text{Eu}_{(\text{aq})}^{+3}$ led him to conclude that the aquo-complex was eightfold coordinate. The most general studies of the aquo-complexes of the lanthanides have been carried out by Spedding and his associates⁴⁹⁻⁵⁶. The variations with atomic number of apparent volumes and viscosities of lanthanide chloride solutions suggest that nine water molecules are bound by the 3+ ions from La to Nd, and that eight are bound from Tb^{3+} to Yb^{3+} . For the remaining rare earth ions the aquo coordination lies between eight and nine.

Oxides

Among the solid oxides, the relatively rare monoxides, such as EuO and AmO , display the NaCl type of structure with sixfold oxygen coordination, in essential agreement with the expectations from radius-ratio considerations. Cubic, hexagonal and monoclinic sesquioxides are observed in both the lanthanide and actinide elements. The former are similar in structure to the fluorite-type dioxides, but the coordination number is reduced to six because of vacancies in the anion lattice. In the hexagonal (A) and monoclinic (B) forms of the sesquioxides, the metal atoms are not equivalent and the coordination may be described as both sixfold and sevenfold.

The dioxides of the lanthanides and actinides invariably exist in the cubic, fluorite-type structure with eightfold coordination. This structure is highly persistent, in spite of the apparently unfavourable radius ratio.

In the stoichiometrically well-defined oxide, Pa_2O_5 , there are different kinds of Pa atoms in the unit cell, in which one kind is eightfold, and the other sevenfold coordinate. Eightfold coordination is exhibited in UO_2^{2+} , with a distinct linear $\text{O}-\text{U}-\text{O}$ group with shortened $\text{U}-\text{O}$ distances, and six additional oxygens in a hexagonal array in the equatorial plane perpendicular to and bisecting the $\text{O}-\text{U}-\text{O}$ axis.

In summary, in their oxides, the lanthanide and actinide elements tend to exhibit coordination numbers of six or seven in the 2+ and 3+ states, and seven or eight in their higher oxidation states.

Fluorides

Binary fluorides of the actinide and lanthanide element range in composition from MF_2 to MF_6 . The difluorides exhibit the fluorite structure with coordination number eight⁵¹. The lanthanide and actinide trifluorides may

occur in one or more of three structures, two of which are hexagonal, and the third orthorhombic.

In one hexagonal form (YF_3 type), the fluoride coordination about the cation is nine, with eight fluorides at approximately equal distances, and the ninth 0.3 Å farther out⁵². Ninefold fluoride coordination is observed also in the complex salt $NaNdF_4$. The fluoride arrangement about the cation is hexagonal bipyramidal⁵³. The actinide and lanthanide tetrafluorides are isostructural with ZrF_4 . Fluoride coordination is eightfold, arranged about the cation in a slightly distorted square antiprism⁵⁴ but in the complex salt $LiUF_5$, the coordination increases to nine⁵⁵.

Simple fluorides of the penta positive state of the actinides include α and β UF_5 , and PuF_5 . In α - UF_5 and PuF_5 sixfold fluoride coordination occurs in an octahedral arrangement⁵⁶. It has been suggested that in β UF_5 , which is isostructural with PaF_5 , seven fluoride atoms are coordinated to the Pa atom⁵⁶. In the complex compounds, K_2PaF_7 , $RbPaF_6$ and $CsUF_6$, the fluoride coordination decreases from nine⁵⁷ to eight⁵⁸ to six⁵⁹, respectively. In the latter, the fluorides are disposed at the apices of a slightly distorted octahedron.

The simple actinide hexafluorides, UF_6 , NpF_6 and PuF_6 are monomeric in the vapour state, exhibit sixfold fluoride coordination, and a perfectly octahedral arrangement of the fluorides. Some distortion of the octahedra occurs in the solids, but these are essentially molecular compounds, with low heats of vaporization⁶⁰. In the complex salt, Na_2UF_8 , the fluoride coordination increases to eight, with all fluorine distances equal⁶¹.

Chlorides

The lanthanide dichlorides, $NdCl_2$, $SmCl_2$ and $EuCl_2$ exhibit the orthorhombic $PbCl_2$ structure type with sevenfold coordination⁶². Dysprosium and ytterbium dichlorides also exhibit an orthorhombic structure, but this has not been characterized⁶³.

The lanthanide and actinide trichlorides exhibit one or more of the three types of structures designated as: the UCl_3 type, the $PuBr_3$ type of structure, $AlCl_3$ type. The trichlorides from La to Gd exhibit the UCl_3 type of structure, $TbCl_3$ is of the orthorhombic $PuBr_3$ type, and the remaining rare earth trichlorides are monoclinic, $AlCl_3$ type structures. The known actinide trichlorides, including $EsCl_3$ are of the UCl_3 type, as is to be expected from a comparison of lanthanide and actinide ionic radii.

In the UCl_3 type of structure, nine chlorine atoms are bonded to the central cation. Three equidistant chlorines are arranged in the equatorial plane of the cation at the vertices of an isosceles triangle, while the remaining six chlorines at a somewhat different distance are distributed equally in triangular array at each pole⁶⁴.

In the $PuBr_3$ structure the halide coordination is reduced to eight⁶⁵. Further decrease in the cation-anion radius ratio, caused by the lanthanide contraction, reduces the coordination number to six, with the anions in a distorted octahedral arrangement⁶⁶. In the complex chloride, $Cs_2NaM^{III}Cl_6$, where M^{III} is a lanthanide or actinide tripositive ion, six chlorides are arranged in an octahedron about the cation⁵.

The actinide tetrachlorides $ThCl_4$, $PaCl_4$, UCl_4 and $NpCl_4$ are iso-

structural with eight atoms arranged about the M(IV) atom, at the corners of a distorted cube. In ThCl_4 , four chloride atoms are at 2.46 Å and the remaining four at 3.11 Å from the central thorium atom⁶⁷. In the complex chloride Cs_2PuCl_6 , an octahedron of six chlorine atoms surrounds each plutonium⁶⁸.

Simple binary pentachlorides are formed by uranium and protactinium. In the former, the dimeric units, U_2Cl_{10} exist in the solid; the approximately octahedrally distributed chlorine atoms about each uranium atom share an edge. The coordination number of the pentapositive uranium atom, therefore, is six⁶⁹. In PaCl_5 , the arrangement of chlorides is pentagonal bipyramidal⁷⁰, corresponding to coordination number seven. The only simple binary chloride formed by a 6+ actinide is UCl_6 . The structure is typically molecular with six chlorine atoms arranged about each uranium in almost perfect octahedral array⁷¹.

A great variety of hexavalent oxychlorocomplexes of the actinides exists, and uranyl chloride, UO_2Cl_2 , reacts with a variety of oxygen and nitrogen donor ligands³, but the structures of these substances are not known. Among the relatively few structures determined for compounds of the actinide or lanthanide elements with organic ligands are $\text{NaUO}_2(\text{CH}_3\text{COO})_3$,

$$\begin{array}{c} \text{O} \quad \text{H} \quad \text{O} \\ \parallel \quad | \quad | \\ \text{Th}(\text{CH}_3-\text{C}-\text{C}=\text{C}-\text{CH}_3)_4 \end{array}$$

and the corresponding tetrakis(acetylacetonato) uranium(IV) compound, and the recently discovered cyclooctatetraene compounds of uranium, thorium, neptunium and plutonium mentioned earlier. It was shown by Zachariasen and Plattinger⁷² that in $\text{Na}(\text{UO}_2)(\text{CH}_3\text{COO}^-)_3$, the linear O—U—O grouping is surrounded by a hexagon of six acetate oxygens in the equatorial plane perpendicular to the O—U—O chain. The oxygen ring is slightly puckered with respect to the equatorial plane. Uranium(IV) and thorium(IV) acetyl acetonates have been found to be isostructural. In the thorium compound, the eight oxygens are arranged about the thorium in the form of Archimedian antiprism⁷³.

We may summarize the foregoing survey of the coordination behaviour of the actinides and lanthanides by noting that strong evidence exists for the coordination of eight or nine molecules of water in the 3+ aquo ions. No data are available regarding the coordination of water by the ions of other oxidation states. In the simple oxides, chlorides and fluorides, coordination numbers vary from six to nine, with larger halide coordination being observed in the lighter (and larger) ions at the beginning of each transition series. Sixfold, or lower, coordination, which is so prominent in the *d* transition element complexes, is relatively rare in the *f* transition elements. The coordination behaviour departs from hard-sphere radius ratio rules particularly in the dioxides and chlorides and (covalently bonded?) 5+ and 6+ compounds of the actinides.

VIII. STABILITIES OF COMPLEXES OF THE LANTHANIDE AND ACTINIDE ELEMENTS

In their reviews of the coordination chemistry of the actinides, both Comyns¹ and Bagnall³ concluded that in the tripositive state the coordination

chemistry of the actinides is very similar to that of the rare earths. There is no reason to alter this conclusion on the basis of evidence available at the present time. In his exhaustive review of the coordination chemistry of the rare earths, Moeller² commented that the lanthanide elements were reluctant to form true coordination compounds, and did so only with very strong donor ligands or powerful chelating agents. The lanthanide and actinide elements may, therefore, be classed as Chatt–Ahrland type a elements, provided we refer to their behaviour in the tripositive state. Enhanced complexing ability may be expected from the tetrapositive actinide ions; regrettably, these have not been studied to the same extent as the 3+ ions.

The tripositive ions of both the lanthanide and actinide elements exhibit variations in their ion exchange or solvent extraction behaviour as a function of atomic number, in ways which have challenged definitive explanation for a number of years. Various effects such as the stronger influence of *f* orbital bonding in the early actinides⁷⁴ or crystal field interactions⁷⁵ have been suggested to explain the observed phenomena. Some of the most careful studies of this kind have been carried out by Polish scientists, especially Dr I. Fidelis and her collaborators^{76–80}. These workers have made very careful studies of the separation factor α between adjacent pairs of lanthanide elements in solvent extraction or ion exchange processes. They have discovered that the α values tend to persist, regardless of change of ligand. The examples of this phenomenon are so numerous as to establish the reality of the effect beyond any question. With much insight into the possible cause of the observed variations, they carefully studied the precise values of the lattice parameters of the rare earth sesquioxides, which had been measured by Templeton and Dauben¹⁷, and found excellent correlation when the differences in ionic radii between adjacent rare earths were plotted in the same way. This illustrates the important fact that in the tripositive lanthanides, ligand–metal interactions are largely coulombic in nature. A change of only a few thousandths of an Ångström in the ion–ligand distance can change the coulombic energy by enough (about 400 cal mol⁻¹) to increase or decrease a distribution coefficient by a factor of two.

In the search for explanations for the variations with atomic number of extraction or ion exchange behaviour of the 4*f* or 5*f* elements, it is essential not to overlook the importance of having very exact information about cation–ligand distances.

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