TOPICS IN INORGANIC AND GENERAL CHEMISTRY

MONOGRAPH 4

N. E. TOPP

THE CHEMISTRY OF THE RARE-EARTH ELEMENTS

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ELSEVIER PUBLISHING COMPANY
AMSTERDAM / LONDON / NEW YORK
1965

ELSEVIER PUBLISHING COMPANY
335 JAN VAN GALENSTRAAT, P.O. BOX 211, AMSTERDAM

AMERICAN ELSEVIER PUBLISHING COMPANY, INC.
52 VANDERBILT AVENUE, NEW YORK, N.Y. 10017

ELSEVIER PUBLISHING COMPANY LIMITED
RIPPLESIDE COMMERCIAL ESTATE
BARKING, ESSEX

LIBRARY OF CONGRESS CATALOG CARD NUMBER 65-12563

WITH 21 ILLUSTRATIONS AND 22 TABLES

PRINTED IN THE NETHERLANDS

Preface

The rare earths are a fascinating group of elements, which have only recently become widely available in a state of high purity. The separation of these elements from one another was at one time regarded as one of the most difficult problems in classical inorganic chemistry. When the rare earth elements were identified as fission products from uranium, it became imperative to obtain more accurate physical data on the group, and this fact stimulated a large amount of work on modern separation techniques which was mainly carried out in the United States. An outcome of the success of this work has been the ready availability of the lanthanides for the first time, and as a result the past ten years has seen a notable increase in the knowledge of their chemical and physical properties.

I had spent several years working on various aspects of the separation problem when Dr. J. S. ANDERSON suggested that I should write a book on the chemistry of these elements. During my own work I had become aware of the need for an up-to-date reference book. In this book, I have endeavoured to review the known chemistry of these elements to the beginning of 1964. After a brief historical discussion of the discovery of the elements, their geochemistry and position in the periodic system are considered. Some typical methods of extracting the elements from minerals are described, and these are followed by a discussion of the more important separation techniques. In the following chapters, compounds of the lanthanides, and their properties, are discussed. The compounds fall into two categories, halides and salts with oxo-anions which are mostly soluble in water, and compounds such as oxides which are only known in the solid state. This is followed by a description of the analytical methods of lanthanide chemistry. In conclusion, a chapter is devoted to a consideration of the methods used in preparing the lanthanide metals and of their more important physical properties, followed by descriptions of a number of applications of these elements.

It has been my good fortune to be able to discuss many points which arose during the preparation of the manuscript with colleagues at Teddington, both in the National Chemical Laboratory and the National Physical Laboratory. I would like in particular to thank Drs. M. H. FORD-SMITH and C. R. VEALE for their critical comments on various sections of the text. The preparation of the manuscript has also been greatly assisted by Professor P. L. ROBINSON, whose constructive criticism has been of the utmost value. I should also like to express my collective thanks to the authors of a number of publications, and to their publishers, for permission to reproduce diagrams; individual acknowledgement is made in the text.

Finally, I must thank my wife for her help in preparing the manuscript, and Mrs. J. TAYLOR for typing the final draft.

Teddington, July, 1964. N. E. TOPP

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CHAPTER 1

Introduction

DISCOVERY OF THE RARE EARTH ELEMENTS OR LANTHANIDES

The rare earth elements are the largest naturally occurring group in the periodic system. Although in fact they are not at all rare, the close similarity of their chemical and physical properties made the occurrence of several of them together in individual minerals almost inevitable, and also accounted for the considerable difficulties in separating them from one another. Indeed for many years the separation of the rare earth elements was rightly considered to be one of the most difficult problems in inorganic chemistry It is not surprising that over one hundred years elapsed between the isolation and recognition of an element like the rare earths, yttrium in 1794, and the discovery of lutetium in 1907. In the interval, nearly one hundred alleged elements presumed to belong to this group were reported most of which were eventually eliminated entirely on chemical evidence. In 1913 MOSELEY showed there were fourteen atomic numbers between lanthanum and hafnium, and this set an upper limit to the discoverable rare earth elements. Of these, all were identified and prepared to a certain degree of purity by 1907 except promethium (atomic number 61). This element was not isolated until 1948 when MARINSKY and CORYELL, using the new technique of ion-exchange chromatography, obtained it from uranium fission products.[1] The element is radioactive and an inactive isotope of promethium is unknown.

The atomic weights and isotopes of the rare earth elements are summarised in Table 1.[2] Although they are not rare earth elements, scandium and yttrium are included since they are precursors of the rare earth family in Group III of the Periodic Table. Both

TABLE 1

Element	*Symbol*	*Atomic Number*	*Atomic Weight*	*Isotopes*
Scandium	Sc	21	44.956	45
Yttrium	Y	39	88.905	89
Lanthanum	La	57	138.91	138, 139
Cerium	Ce	58	140.12	136, 138, 140, 142
Praseodymium	Pr	59	140.907	141
Neodymium	Nd	60	144.24	142, 143, 144, 145, 146, 148, 150
Promethium	Pm	61		—
Samarium	Sm	62	150.35	144, 147, 148, 149, 150, 152, 154
Europium	Eu	63	151.96	151, 153
Gadolinium	Gd	64	157.25	152, 154, 155, 156, 157, 158, 160
Terbium	Tb	65	158.924	159
Dysprosium	Dy	66	162.50	156, 158, 160, 161, 162, 163, 164
Holmium	Ho	67	164.930	165
Erbium	Er	68	167.26	162, 164, 166, 167, 168, 170
Thulium	Tm	69	168.934	169
Ytterbium	Yb	70	173.04	168, 170, 171, 172, 173, 174, 176
Lutetium	Lu	71	174.97	175, 176

elements are found in rare earth minerals, although scandium is rarely present in more than marginal quantity.

The terms "light", "heavy", and "middle" earths will be frequently used in this book. Although the terms are imprecise they are very convenient; by light earths is meant the elements from lanthanum to europium; similarly the heavy earths comprise gadolinium to lutetium; and the middle earths samarium to holmium. Yttrium is always present in the more important rare earth minerals, and is often a major constituent if the mineral contains the middle or heavy earth groups (p. 16). As many of its chemical properties are similar to those of the heavy earth elements, its chemistry will be discussed. Scandium, however, differs from yttrium and the lanthanides in some respects and its chemistry will not be considered.

Turning back to the discovery of yttria, GADOLIN isolated this element from gadolinite in 1794, a mineral now known to contain predominantly yttrium and the middle and heavy earths. Soon after this, in 1804, BERZELIUS and HISINGER examined cerite expecting to isolate yttria from the mixed silicate. Instead they found a new oxide and named it ceria. Cerite in its turn is now known to be made up of mainly the light earths. Both GADOLIN's "yttria" and BERZELIUS' "ceria" were later shown to be complex mixtures of oxides, and these two mixtures each provided a starting material from which the light and heavy earth groups were subsequently isolated.

MOSANDER pyrolysed the crude material termed "ceria nitrate", and extracted from the ignited residue with dilute nitric acid a new earth, lanthana (1839). Two years later (1841) he isolated a second earth, didymia, from lanthana itself. He then turned to Gadolin's yttria, and found it to be even more complex. By fractional precipitation with ammonia, he succeeded in obtaining three earths; yttria, terbia, and erbia (1843).

Nearly forty years later, DE MARIGNAC extracted a new earth, ytterbia, from MOSANDER's erbium nitrate (1878). It was from this ytterbia that NILSON isolated the oxide of the first member of

TABLE 2

Element	*Symbol*	*Atomic Number*	*Descriptive Classification*
Lanthanum	La	57	
Cerium	Ce	58	
Praseodymium	Pr	59	
Neodymium	Nd	60	LIGHT EARTHS
Promethium	Pm	61	
Samarium	Sm	62	
Europium	Eu	63	
Gadolinium	Gd	64	MIDDLE EARTHS
Terbium	Tb	65	
Dysprosium	Dy	66	
Holmium	Ho	67	HEAVY EARTHS
Erbium	Er	68	
Thulium	Tm	69	
Ytterbium	Yb	70	
Lutetium	Lu	71	

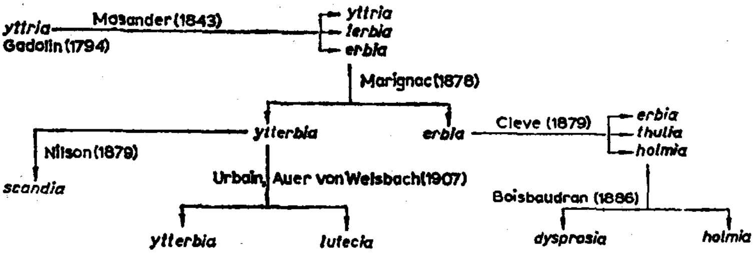

Fig. 1. Discovery of the heavy earth elements: separation of the heavy earths from yttria. [Reproduced, with permission, from *Research*, 11 (1958) 376.]

Group IIIA, scandia, which excited considerable interest at the time since its properties proved to be those required by MENDELEEV's predicted "ekaboron" (1879). Two further constituents of "erbia", thulia and holmia, were separated by CLEVE (1879), and soon after DE BOISBAUDRAN produced a third constituent, dysprosia (1886). More than twenty years later, URBAIN and VON WELSBACH independently obtained lutetia from ytterbia (1907). DE MARIGNAC also believed that Mosander's didymia was complex, and DE BOISBAUDRAN proved this was so by separating from it samaria in 1879 and gadolinia in 1886. VON WELSBACH isolated neodymium and praseodymium from didymium, by fractional crystallisation

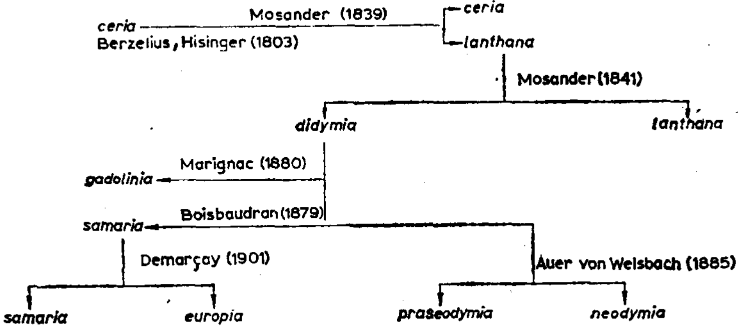

Fig. 2. Discovery of the light earth elements: separation of the light earths from ceria. [Reproduced, with permission, from *Research*, 11 (1958) 376.]

of the double ammonium nitrates. Finally, a similar procedure applied to the "samarium" magnesium nitrates led to the discovery of europium by DEMARCAY (1901). From 1850 onwards, the development of spectroscopic techniques greatly assisted identification of the various species. VON WELSBACH, who had worked with BUNSEN, made important contributions to the spectroscopy of the lanthanide elements.

In the early days, the accommodation of the rare earth elements in the Periodic Table proved to be a completely insoluble problem. There was uncertainty about their number and a Periodic Table based on groups and sub-groups which owed their existence to physical and chemical properties provided obvious places for only one such element, that now occupied by lanthanum. However, MOSELEY's atomic numbers solved this and other problems of the classification of the elements. In retrospect, the earlier work on separating the rare earth elements seems truly heroic, particularly when the limitations of the techniques and effort available are realised. It is, perhaps, fitting that the last of these elements, promethium, was isolated by a new means that has now supplanted the older methods of separation.

DISTRIBUTION OF THE RARE EARTH ELEMENTS IN NATURE

GOLDSCHMIDT's data on the abundance of the lanthanide elements in igneous rocks are summarised in Table 3, columns 1-3. For comparison, columns 4-6 show figures for the abundance of a number of other better known elements, not all of which would be considered rare.[3] It should be borne in mind that there is a tendency for elements to become less abundant with increase in atomic number.[4] Also, the abundances of the lanthanides given in Table 3 are all minute compared with the abundance of aluminium, which is 8.8×10^4 g/tonne.

Clearly, yttrium and cerium are by no means rare, being about as abundant as zinc and cobalt. Next come neodymium and lanthanum which run somewhat above the level of lead. The occur-

TABLE 3

COMPARISON OF ABUNDANCE OF LANTHANIDES AND OTHER ELEMENTS IN IGNEOUS ROCKS

Element	*Atomic number*	*Abundance, g/tonne*	*Element*	*Atomic number*	*Abundance, g/tonne*
Y	39	31	Be	4	6
La	57	19	Co	27	40
Ce	58	44	Ni	28	100
Pr	59	5.6	Cu	29	100
Nd	60	24	Zn	30	40
Pm	61	—	Ga	31	15
Sm	62	6.5	As	33	5
Eu	63	1	Nb	41	15
Gd	64	6.3	Mo	42	15
Tb	65	1	Ag	47	0.1
Dy	66	4.3	Cd	48	0.5
Ho	67	1.2	Pt	78	0.005
Er	68	2.4	Au	79	0.005
Tm	69	0.3	Hg	80	0.5
Yb	70	2.6	Pb	82	16
Lu	71	0.7	Bi	83	0.2

rence of many other lanthanides is greater than that of beryllium and arsenic, and even europium exceeds silver and bismuth in abundance. Clearly, the lanthanide elements as a whole never qualified as rare elements and this has become increasingly clear as the methods for bringing them into a pure state have been so notably improved.

ELECTRONIC STRUCTURES OF THE RARE EARTH ELEMENTS

Of the lanthanide elements, lanthanum has a natural place in Group III A of the Periodic Table. Above it are scandium and yttrium, and below it is the element actinium. The four elements have many chemical similarities and are respectively the first members of the four series of transition elements, these being made up of elements with unfilled lower orbitals. In the first two transition series there are unfilled d-orbitals and in the last two which comprise the lanthanides and the actinides respectively there are unfilled f-orbitals.

The determination of the electronic configuration of a lanthanide or an actinide element is very difficult. The classical method depends upon a term analysis of the emission spectrum of the element.[5] The spectra of the lanthanides are exceedingly complex, and such an analysis has so far been made for only eight of these elements.[6-9] Results deduced from spectroscopy have been confirmed and supplemented by deductions from atomic beam resonance.[10-12] This method depends upon direct measurement of the electronic angular momentum, and the atomic g-values of

TABLE 4

ELECTRONIC CONFIGURATION OF THE LANTHANIDE ELEMENTS

	Atomic Number	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s
Sc	21	2	2	6	2	6	1	2							
Y	39	2	2	6	2	6	10	2	6	1		2			
La	57	2	2	6	2	6	10	2	6	10		2	6	1	2
Ce*	58	2	2	6	2	6	10	2	6	10	1	2	6	1	2
Pr	59	2	2	6	2	6	10	2	6	10	3	2	6		2
Nd	60	2	2	6	2	6	10	2	6	10	4	2	6		2
Pm	61	2	2	6	2	6	10	2	6	10	5	2	6		2
Sm	62	2	2	6	2	6	10	2	6	10	6	2	6		2
Eu	63	2	2	6	2	6	10	2	6	10	7	2	6		2
Gd	64	2	2	6	2	6	10	2	6	10	7	2	6	1	2
Tb*	65	2	2	6	2	6	10	2	6	10	9	2	6		2
Dy	66	2	2	6	2	6	10	2	6	10	10	2	6		2
Ho	67	2	2	6	2	6	10	2	6	10	11	2	6		2
Er	68	2	2	6	2	6	10	2	6	10	12	2	6		2
Tm	69	2	2	6	2	6	10	2	6	10	13	2	6		2
Yb	70	2	2	6	2	6	10	2	6	10	14	2	6		2
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1	2

* The configurations of cerium and terbium are still uncertain.

the atoms, from which the ground states can be deduced. Present views on the electronic structures are given in Table 4.

The nuclear charge increases in proton units, and with this increase successive electrons are added to the least energetic of the available orbitals. Considering first the Group IIIA elements scandium and yttrium, these have respectively the argon core with ($3d^1 4s^2$) outer electrons and the krypton core with ($4d^1 5s^2$) outer electrons. In their usual charge state of +3, the ions have the Ar and Kr configurations. After scandium, ten electrons are added to the 3d shell, and similarly after yttrium ten electrons are added to the 4d shell to give the first and second series of transition elements. However, in the third long period, the 5s- and 5p-orbitals have already been filled at xenon ($Z = 54$). Commencing with cerium, 14 electrons are added successively to the 4f shell to give the sequence of lanthanide elements; a similar addition of 5f electrons commences after actinium. The peculiarities of the lanthanide elements derive very largely from the deep-lying 4f electrons. Unlike the 3d and 4d electrons of the first and second transition series which project to the periphery of the atoms and thereby determine the possible valency states, the 4f electrons are shielded by eight electrons, $5s^2$ and $5p^6$, so that their chemical significance is so slight as to allow the remarkable similarity of the lanthanides.

The 4f electrons are not always added singly from cerium to lutetium although there is a tendency for the electron to enter the 4f shell rather than the 5d shell. The configurations of cerium and terbium are uncertain, but it is established that the 4f shell is half-filled at europium and filled at ytterbium. The normal charge state of the lanthanide elements is three, and the terpositive ions are formed by losing the $6s^2$ and generally a 4f electron, but sometimes the $5d^1$ electron. Thus the terpositive ion has the xenon core with 4f electrons. It is significant that no charge state other than three is known for lanthanum, gadolinium and lutetium. Some of the lanthanide elements have charge states of two or four, the ionic configurations being (Xe) $4f^{n+1}$ and (Xe) $4f^{n-1}$ respectively (p. 69). However, recent work has demonstrated that these higher and lower charge states are not confined to the elements immediately adjacent to lanthanum, gadolinium, and lutetium. It has been long argued that the unusual valency states are associated with the extra stability of the empty, the half-filled, and the filled 4f configurations, but it is now known that these oxidation states are more widely distributed and cannot be accounted for by this explanation alone.

MAGNETIC PROPERTIES

In common with many of the transition elements, most of the lanthanide metals and their compounds are strongly paramagnetic,* that is, they tend to align themselves parallel to a magnetic field. Paramagnetism is always associated with the presence of unpaired electrons, which make spin and orbital contributions to the magnetic moment. In the first and second transition series, the unpaired electrons lie in the 3d or 4d electron shells, but in the lanthanide elements they are in the 4f shell. It has already been stated that the 4f electrons do not take part in chemical bonding, since they are

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* Paramagnetic substances are more permeable to a magnetic field than a vacuum, and the converse is true of diamagnetic substances. These properties are determined by measuring the force exerted on test samples by magnetic fields of known intensity. Thus, if a specimen is placed in a magnetic field of strength H, the relation between the field strength and the magnetic induction is:— $B = H + 4\pi I$ where I is the intensity of magnetization. The quantity $I/H = K$ is the volume susceptibility; the term χ_m is used to denote the molal susceptibility. A convenient unit for expressing magnetic moments is the Bohr magnetion, β,

$$\beta = \frac{eh}{4\ mc} = 0.917 \times 10^{-20}\ \text{erg/gauss}$$

where e is electronic charge, h Plancks' constant, m the mass of the electron and c the velocity of light.

The magnetic susceptibility of many paramagnetic substances varies inversely with temperature according to the Curie-Weiss law:

$$\chi_m = \frac{c}{T + \theta}$$

where χ_m is the molal susceptibility, c is a constant, T the temperature of measurement, and θ the Curie temperature.