

# Gmelin Handbuch der Anorganischen Chemie

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## Sc, Y, La–Lu RARE EARTH ELEMENTS

Part D 1

Coordination Compounds

# Gmelin Handbuch der Anorganischen Chemie

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## Preface

This volume, Volume D 1, begins with a general survey of the complexes of scandium, yttrium, and the rare earth elements lanthanum-lutetium. The pertinent properties of the ions are discussed first, primarily as they are related to atomic and ionic ground-state electronic configurations. Factors affecting complexations are discussed, and general properties of complex species, specifically molecular geometry, coordination number, thermodynamic and kinetic stability, and bonding, are then described.

In subsequent chapters, complexes are grouped into major classifications by donor atom type. Within each major classification, sub-classes are used to describe the species formed by specific donor ions or molecules. Where thermodynamic data, formation constants, and/or kinetic data are available for the complexation reactions, these are presented before the syntheses and properties of isolated complexes.

Chapter 2 describes complexes with nitrogen donor ligands. The majority of these species are derived from the trivalent ions ( $M^{III}$ ). Where  $M^{II}$  or  $Ce^{IV}$  complexes have been reported for a specific ligand, they are described after the  $M^{III}$  complexes. The ligands include ammonia, hydrazine, amines, polyamines, and heterocyclic amines and polyamines. Both solution studies and the syntheses and properties of isolated compounds are described.

Chapter 3 describes some of the complexes derived from ligands that contain both nitrogen and oxygen donor atoms. Examples of ligands of this type are amino acids, amine-N-polycarboxylic acids, aromatic and N-heterocyclic amine carboxylic acids, hydrazinecarboxylic acids, hydrazine-polycarboxylic acids. Most of these complexes have been studied in solution. A limited number have been isolated and investigated.

This volume is supplemented by a formula index listing all ligands and their molecular formulas.

The remaining complexes containing ligands with both nitrogen and oxygen donor atoms will be discussed in Volume D 2. Complexes containing ligands with only oxygen donor atoms and with other donor atoms and the organometallic compounds of the rare earth elements will be described in Volumes D 2 and D 3.

Tempe, Arizona, USA  
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December 1979

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Edith Schleitzer-Rust

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## Complexes of the Rare Earth Elements

*Complexes  
of the  
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## 1 Introduction

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*Introduction*

*Rare Earth  
Element  
Ions.  
General  
Properties*

### 1.1 Rare Earth Element Ions. General Properties

The rare earth elements, including scandium and yttrium, are best characterized and distinguished from the other elements in terms of their atomic and ionic ground-state electronic configurations (Table 1/1) and those properties that can be related, directly or indirectly, to these configurations. Properties pertinent to the complexation process and the characteristics of complexes include oxidation states, crystal radii, energy states, magnetic and spectroscopic behavior, bonding, coordination number and molecular geometry, and thermodynamic and kinetic stability.

Table 1/1

Electron configurations and levels of the lanthanide atoms and ions in their ground states.

Atomic No.	M	M <sup>0</sup>	M <sup>+</sup>	M <sup>2+</sup>	M <sup>3+</sup>
21	Sc	3d <sup>1</sup> 4s <sup>2</sup> 2D <sub>3/2</sub>			3d <sup>0</sup> 1S <sub>0</sub>
39	Y	4d <sup>1</sup> 5s <sup>2</sup> 2D <sub>3/2</sub>			4d <sup>0</sup> 1S <sub>0</sub>
57	La	5d 6s <sup>2</sup> 2D <sub>3/2</sub>	5d <sup>2</sup> 3F <sub>2</sub>	5d 2D <sub>3/2</sub>	5p <sup>6</sup> 1S <sub>0</sub>
58	Ce	4f 5d 6s <sup>2</sup> 1G <sub>4</sub> <sup>o</sup>	4f 5d <sup>2</sup> 4H <sub>7/2</sub> <sup>o</sup>	4f <sup>2</sup> 3H <sub>4</sub>	4f 2F <sub>5/2</sub> <sup>o</sup>
59	Pr	4f <sup>3</sup> 6s <sup>2</sup> 4I <sub>9/2</sub> <sup>o</sup>	4f <sup>3</sup> 6s (9/2, 1/2) <sub>4</sub> <sup>o</sup>	4f <sup>3</sup> 4I <sub>9/2</sub> <sup>o</sup>	4f <sup>2</sup> 3H <sub>4</sub>
60	Nd	4f <sup>4</sup> 6s <sup>2</sup> 5I <sub>4</sub>	4f <sup>4</sup> 6s (4, 1/2) <sub>7/2</sub>	4f <sup>4</sup> 5I <sub>4</sub>	4f <sup>3</sup> 4I <sub>9/2</sub> <sup>o</sup>
61	Pm	4f <sup>5</sup> 6s <sup>2</sup> 6H <sub>5/2</sub> <sup>o</sup>	4f <sup>5</sup> 6s 7H <sub>2</sub> <sup>o</sup>	4f <sup>5</sup> 6H <sub>5/2</sub> <sup>o</sup>	4f <sup>4</sup> 5I <sub>4</sub>
62	Sm	4f <sup>6</sup> 6s <sup>2</sup> 7F <sub>0</sub>	4f <sup>6</sup> 6s 8F <sub>1/2</sub> <sup>o</sup>	4f <sup>6</sup> 7F <sub>0</sub>	4f <sup>5</sup> 6H <sub>5/2</sub> <sup>o</sup>
63	Eu	4f <sup>7</sup> 6s <sup>2</sup> 8S <sub>7/2</sub> <sup>o</sup>	4f <sup>7</sup> 6s 9S <sub>4</sub> <sup>o</sup>	4f <sup>7</sup> 8S <sub>7/2</sub> <sup>o</sup>	4f <sup>6</sup> 7F <sub>0</sub>
64	Gd	4f <sup>7</sup> 5d 6s <sup>2</sup> 9D <sub>2</sub> <sup>o</sup>	4f <sup>7</sup> 5d 6s 10D <sub>5/2</sub> <sup>o</sup>	4f <sup>7</sup> 5d 9D <sub>2</sub> <sup>o</sup>	4f <sup>7</sup> 8S <sub>7/2</sub> <sup>o</sup>
65	Tb	4f <sup>9</sup> 6s <sup>2</sup> 6H <sub>15/2</sub> <sup>o</sup>	4f <sup>9</sup> 6s 7H <sub>8</sub> <sup>o</sup>	4f <sup>9</sup> 6H <sub>15/2</sub> <sup>o</sup>	4f <sup>8</sup> 7F <sub>6</sub>
66	Dy	4f <sup>10</sup> 6s <sup>2</sup> 5I <sub>8</sub>	4f <sup>10</sup> 6s (8, 1/2) <sub>17/2</sub>	4f <sup>10</sup> 5I <sub>8</sub>	4f <sup>9</sup> 6H <sub>15/2</sub> <sup>o</sup>
67	Ho	4f <sup>11</sup> 6s <sup>2</sup> 4I <sub>15/2</sub> <sup>o</sup>	4f <sup>11</sup> 6s (15/2, 1/2) <sub>8</sub> <sup>o</sup>	4f <sup>11</sup> 4I <sub>15/2</sub> <sup>o</sup>	4f <sup>10</sup> 5I <sub>8</sub>
68	Er	4f <sup>12</sup> 6s <sup>2</sup> 3H <sub>6</sub>	4f <sup>12</sup> 6s (6, 1/2) <sub>13/2</sub>	4f <sup>12</sup> 3H <sub>6</sub>	4f <sup>11</sup> 4I <sub>15/2</sub> <sup>o</sup>
69	Tm	4f <sup>13</sup> 6s <sup>2</sup> 2F <sub>7/2</sub> <sup>o</sup>	4f <sup>13</sup> 6s (7/2, 1/2) <sub>4</sub> <sup>o</sup>	4f <sup>13</sup> 2F <sub>7/2</sub> <sup>o</sup>	4f <sup>12</sup> 3H <sub>6</sub>
70	Yb	4f <sup>14</sup> 6s <sup>2</sup> 1S <sub>0</sub>	4f <sup>14</sup> 6s 2S <sub>1/2</sub>	4f <sup>14</sup> 1S <sub>0</sub>	4f <sup>13</sup> 2F <sub>7/2</sub> <sup>o</sup>
71	Lu	4f <sup>14</sup> 5d 6s <sup>2</sup> 2D <sub>3/2</sub>	4f <sup>14</sup> 6s <sup>2</sup> 1S <sub>0</sub>	4f <sup>14</sup> 6s 2S <sub>1/2</sub>	4f <sup>14</sup> 1S <sub>0</sub>

The ground-state atomic configurations of the scandium, yttrium, and lanthanum atoms are of the type [noble gas core] (n-1)d<sup>1</sup>ns<sup>2</sup> (n=4 for Sc, 5 for Y, 6 for La), those of the other atoms amount essentially to the configuration [La]4f<sup>n</sup>, with n=1 to 14 [1]. The 4f orbitals are comparatively well-buried, and thus substantially shielded from external influences. The ubiquitous +3 state characteristic of the vast majority of the compounds formed by these elements represents a noble-gas core in the ions Sc<sup>3+</sup>, Y<sup>3+</sup>, and La<sup>3+</sup>, but with 4f electrons present in the other species. This preference of +3 state is probably less a consequence of ground-state atomic configurations than of a, perhaps fortuitous, balance between ionization energies and either crystal or solvation energies [2]. The +2 state, although noted for all of the elements in solid binary halides, is limited in solution and in complexes, as a consequence of ready oxidation to the +3 state, to Eu and Yb. The +4 state is limited, as a consequence of ready reduction to the +3 state, to Ce. Thus, the complex ions and compounds are, with but few exceptions, those derived from the M<sup>3+</sup> ions. In the chapters that describe the various types of complexes, those derived from M<sup>3+</sup>, M<sup>2+</sup>, and M<sup>4+</sup> are discussed separately for each ligand.

Due to the imperfect shielding from nuclear attraction of each 4f electron by other 4f electrons the ionic size in a given oxidation state decreases with increasing nuclear charge in the region Z = 57 to 71 (lanthanide contraction [3] (Table 1/2)). For atomic and ionic radii see also Gmelin Handbuch "Seltenerdelemente" B 4, 1976, p. 420. A consequence of this contraction is that the radius of the Ho<sup>3+</sup> ion is the same as that of the Y<sup>3+</sup> ion. However, the Sc<sup>3+</sup> ion is significantly smaller than even the Lu<sup>3+</sup> ion. Paralleling decrease in radii of the M<sup>3+</sup> ions are many increases in thermodynamic stabilities of complexes, increases in covalency in bonding, and decreases in coordination number.

The effective shielding of 4f electrons from external fields by the 5s<sup>2</sup>5p<sup>6</sup> orbital arrangement results in minimal effects on the states the 4f<sup>n</sup> configurations by the surroundings of the M<sup>3+</sup> ions. For a given ion, these effects are thus essentially the same for nearly all compounds of a given ion, both in solution and in the crystalline state [6]. The energy states of the 4f<sup>n</sup> configurations are usefully approximated by the Russell-Saunders scheme, and the spin-orbit coupling constants are comparatively large, see Gmelin Handbuch "Seltenerdelemente" B 4, 1976, p. 131/43, 139. Thus, nearly

every  $M^{3+}$  ion ( $M = \text{La-Lu}$ ) is characterized by a ground state of single  $J$  value and the first excited state which is essentially unpopulated except at very high temperatures. The  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  ions, however, are different in that the first excited state, and for the  $\text{Eu}^{3+}$  ion even the second and third excited states, are close to the ground state and somewhat populated at room temperature.

Properties that are specifically affected are paramagnetism and the absorption and emission of radiant energy. The ions  $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Ce}^{4+}$ , and  $\text{Lu}^{3+}$  are diamagnetic, corresponding to the absence of unpaired electrons. All of the other ions are paramagnetic. However, the spin-only calculation of magnetic moments applicable to the 3d cations is not applicable to these ions. Detailed information is given by Taylor and Darby [7]. That the measured magnetic moments of a number of the complexes discussed in subsequent chapters agree very well with those for the free  $M^{3+}$  ions is indicative of both minimal covalence and lack of participation of 4f electrons in bonding.

Table 1/2

Metallic and crystal radii (Å).

Nuclear Charge	Symbol	Metallic Radius [4]	Crystal Radius [5]		
			+2	+3	+4
21	Sc	1.61		0.73	
39	Y	1.78		0.893	
57	La	1.87		1.061	
58	Ce	1.83		1.034	0.80
59	Pr	1.82		1.013	0.78
60	Nd	1.81		0.995	
61	Pm	ca. 1.81		0.979	
62	Sm	1.80		0.964	
63	Eu	1.99	1.17	0.95	
64	Gd	1.79		0.938	
65	Tb	1.76		0.923	0.76
66	Dy	1.75		0.908	
67	Ho	1.74		0.894	
68	Er	1.73		0.881	
69	Tm	ca. 1.73		0.869	
70	Yb	1.94	0.93	0.858	
71	Lu	1.72		0.848	

The ions  $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ , and  $\text{Lu}^{3+}$  have no absorption bands in the ultraviolet, visible, or infrared regions and are colorless both in crystals and in solution. The  $M^{3+}$  ions,  $\text{Ce}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Yb}^{3+}$  are also colorless, but the first three absorb in the ultraviolet and the last one in the near infrared. All of the other  $M^{3+}$  ions absorb in the visible and are colored, although the pink color of the  $\text{Tb}^{3+}$  ion is very faint. Principal absorption bands and other pertinent data are summarized in Table 1/3, p. 4. Except for the absorption bands of the  $\text{Ce}^{3+}$  and  $\text{Yb}^{3+}$  ions, these absorptions are sharply defined and commonly measurable to one Angstrom unit in width. Except for changes in intensity and very slight changes in wave length, the bands for a particular  $M^{3+}$  ion are essentially the same in crystalline salts, complexes, and solutions. These observations are consistent with normally forbidden, but allowed because of external crystal-field effects, internal transitions within a particular  $4f^n$  configuration [1]. The bands noted for the  $\text{Ce}^{3+}$  and  $\text{Yb}^{3+}$  ions, however, arise from configurational changes involving 5d orbitals and are, as a consequence, more intense and affected by complexation.

Fluorescent emission is particularly characteristic of certain europium(III) complexes and is useful in establishing their molecular structures.

Table 1/3

Absorption bands and colors of  $M^{3+}$  ions.

Ion	Unpaired State Electrons	Principal Absorption Bands (Å)	Color	Principal Absorption Bands (Å)	State	Unpaired Ion Electrons
La <sup>3+</sup>	0 (4f <sup>0</sup> )	<sup>1</sup> S <sub>0</sub> none	colorless	none	<sup>1</sup> S <sub>0</sub>	0 (4f <sup>14</sup> ) Lu <sup>3+</sup>
Ce <sup>3+</sup>	1 (4f <sup>1</sup> )	<sup>2</sup> F <sub>7/2</sub> 2105, 2220, 2380, 2520	colorless	9750	<sup>2</sup> F <sub>7/2</sub>	1 (4f <sup>13</sup> ) Yb <sup>3+</sup>
Pr <sup>3+</sup>	2 (4f <sup>2</sup> )	<sup>3</sup> H <sub>4</sub> 4445, 4690, 4822, 5885	green	3600, 6825, 7800	<sup>3</sup> H <sub>6</sub>	2 (4f <sup>12</sup> ) Tm <sup>3+</sup>
Nd <sup>3+</sup>	3 (4f <sup>3</sup> )	<sup>4</sup> I <sub>9/2</sub> 3540, 5218, 5745, 7395, reddish 7420, 7975, 8030, 8680		3642, 3792, 4870, 5228, 6525	<sup>4</sup> I <sub>11/2</sub>	3 (4f <sup>11</sup> ) Er <sup>3+</sup>
Pm <sup>3+</sup>	4 (4f <sup>4</sup> )	<sup>5</sup> I <sub>4</sub> 5485, 5680, 7025, 7355	pink; yellow	2870, 3611, 4161, 4508, 5370, 6410	<sup>5</sup> I <sub>8</sub>	4 (4f <sup>10</sup> ) Ho <sup>3+</sup>
Sm <sup>3+</sup>	5 (4f <sup>5</sup> )	<sup>6</sup> H <sub>5/2</sub> 3625, 3745, 4020	yellow	3504, 3650, 9100	<sup>6</sup> H <sub>15/2</sub>	5 (4f <sup>9</sup> ) Dy <sup>3+</sup>
Eu <sup>3+</sup>	6 (4f <sup>6</sup> )	<sup>7</sup> F <sub>0</sub> 3755, 3941	colorless*)	2844, 3503, 3677, 4872	<sup>7</sup> F <sub>6</sub>	6 (4f <sup>8</sup> ) Tb <sup>3+</sup>
Gd <sup>3+</sup>	7 (4f <sup>7</sup> )	<sup>8</sup> S <sub>7/2</sub> 2729, 2733, 2754, 2756	colorless	2729, 2733, 2754, 2756	<sup>8</sup> S <sub>7/2</sub>	7 (4f <sup>7</sup> ) Gd <sup>3+</sup>

\*) Tb<sup>3+</sup> may be very pale pink.

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Complexation  
of  $M^{n+}$  ions1.2 Complexation of  $M^{n+}$  ions

Although many complex ions and compounds are described in subsequent chapters, the total number and types of characterized and potentially characterizable species are far less than those derived from the d-transition metals and their ions. Among the factors that are responsible for these differences and thus mitigate against the formation of many complex species are those listed below:

**Electronic Configuration.** The ions Sc<sup>3+</sup>, Y<sup>3+</sup>, La<sup>3+</sup>, and Ce<sup>4+</sup> all have noble-gas atom electronic configurations, like the ions Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>, and thus present no orbitals that could be involved in covalent bond hybridization or interaction. The ions Ce<sup>3+</sup>-Yb<sup>3+</sup>, Sm<sup>2+</sup>, Eu<sup>2+</sup>, and Tb<sup>4+</sup> are characterized by incomplete 4f<sup>14</sup> configurations, which are sufficiently well buried as to preclude the kinds of interaction that are involved with incompletely occupied d orbitals. The ions Yb<sup>2+</sup> and Lu<sup>3+</sup> have Xenon-atom + 4f<sup>14</sup> configurations, which again preclude covalency. Only higher-energy orbitals could thus be involved in covalent linkages, which is possible but uncommon. Ligand-field stabilization energies, where determined, are of the order of only 1 to 2 kcal · mol<sup>-1</sup>. By contrast, the distinguishing orbitals of the d-transition metal ions are valency-shell orbitals, and ligand-field stabilization energies are 100 kcal · mol<sup>-1</sup> or more.

**Ionic Radii.** Each of the cations (M<sup>2+</sup>, M<sup>3+</sup>, or M<sup>4+</sup>) is comparatively large for its charge type, thereby minimizing electrostatic interactions and reducing ionic bond strengths. Among the M<sup>3+</sup> ions, maximum electrostatic interaction is expected for scandium.

**Ligand Exchange.** In those few cases that have been investigated, ligand exchange reactions in aqueous solution have proved to be very rapid. Both the number of species isolable from aqueous systems and the possibilities of isomerism are thus limited. A further complication is that a composition noted for a solid may not persist in solution, and a given complex often is destroyed when recrystallization is attempted.



The water molecule is a particularly strong ligand relative to all the  $M^{2+}$ ,  $M^{3+}$ , and  $M^{4+}$  ions of the rare earth elements and thus either competes strongly for ligand sites or displaces readily other previously bonded ligands. In either a neutral or acidic aqueous environment, competition of this type precludes bonding by any but the strongest ligands and effectively restricts isolable complexes to those formed by chelating ligands. Under alkaline conditions, the hydroxide ion is an even stronger competitor for ligand sites, largely because of the reduced solubilities of the hydrous oxides and/or hydroxides of the  $M^{3+}$  and  $M^{4+}$  ions. This situation is exemplified particularly by ammonia and the amines which, although strong nitrogen-donor species, generate in contact with water sufficient concentrations of hydroxide ion to effect precipitation.

**Donor Atoms.** The cations in question are all typical "A-type acceptors" in the Ahrlund-Chart-Davies sense [1, 2] or "hard acids" in the Pearson sense [3]. By a wide margin, most of the complexes isolable from aqueous systems contain ligands with oxygen-donor sites. Many of these ligands are pure oxygen-donor species; others are mixed oxygen-nitrogen-donor species such as the amine- and polyaminocarboxylates. A limited number of particularly strong nitrogen-donor species which are not themselves extensively hydrolyzable yield pure nitrogen-donor species from aqueous systems. Others coordinate only in the absence of water. Fluoride ion is another strong donor, but relatively few species based upon carbon, sulfur, phosphorus, or heavy halide ion-donors have been described.

These factors indicate that the coordination chemistry of these cations is substantially different from that of the d-transition metal ions.

#### Literature to 1.2:

[1] S. Ahrlund, J. Chart, N. R. Davies (Quart. Rev. [London] 12 [1958] 265/76). — [2] R. J. P. Williams, J. D. Hale (Struct. Bonding [Berlin] 1 [1966] 249/81). — [3] R. G. Pearson (J. Am. Chem. Soc. 85 [1963] 3533/9; J. Chem. Educ. 45 [1968] 581/7, 643/8).

### 1.3 Molecular Geometry and Coordination Number

Contrary to conclusions appearing in the early literature, the coordination number (C.N.) of an  $M^{n+}$  ion, except  $Sc^{3+}$ , in a complex species is rarely six and is commonly larger than six [1 to 3]. Large coordination numbers are consistent with comparatively large ionic radii and lead to a number of molecular geometries. Available experimental data are consistent with (1) the variability in coordination number for a given  $M^{n+}$  ion or a series of ions of the same charge is more dependent upon the spatial accommodation of ligands than upon the bonding properties of ligands and (2) a coordination number in solution commonly differs from a coordination number in a crystal for the same  $M^{n+}$  ion and the same ligand. Definitive data are available only for crystals. Those for solutions are commonly more suggestive than definitive.

The most probable spatial positions occupied by donor atoms relative to central cations  $M^{n+}$  are predictable in terms of Coulombic repulsions involving ligand atoms or electronic pairs and the requirements of maximum symmetry regardless of whether the bonding is ionic or covalent [4 to 7]. Polyhedra, listed in order of preference, and site symmetries so predicted are given below [1]:

C.N. Polyhydra	Site Symmetries	C.N. Polyhydra	Site Symmetries
6 octahedron	( $O_h$ )	8 triangular faced dodecahedron	( $D_{2d}$ )
trigonal prism	( $D_{3h}$ )	square antiprism	( $D_{4d}$ )
7 pentagonal bipyramid	( $D_{5h}$ )	9 tricapped trigonal prism	( $D_{3h}$ )
monocapped octahedron	( $C_{3v}$ )	10 4,4-bicapped square antiprism	( $D_{4d}$ )
monocapped trigonal prism	( $C_{2v}$ )	11 pentacapped trigonal prism	
		12 icosahedron	( $I_h$ )

It is important to realize that among complexes of the rare earth elements the energy of reorganization in going from coordination number 7 to 8, 8 to 9, or 9 to 10 is sufficiently small that solvation upon dissolution of a crystal may readily change the coordination number [4].

In subsequent chapters and for specific ligands, molecular structures are described in detail. The possibilities for isomerism among these large coordination numbers are extensive, but only limited definitive data are currently available.

#### Literature to 1.3:

[1] T. Moeller (MTP [Med. Tech. Publ. Co.] Intern. Rev. Sci. Inorg. Chem. Ser. One 7 [1972] 275/98). — [2] S. P. Sinha (Struct. Bonding [Berlin] 25 [1976] 69/149). — [3] S. P. Sinha (Complexes of the Rare Earths, Pergamon Press, London 1966). — [4] E. L. Muetterties, C. M. Wright (Quart. Rev. [London] 21 [1967] 109/94). — [5] M. G. B. Drew (Progr. Inorg. Chem. 23 [1977] 67/210, 177).

[6] M. G. B. Drew (Coord. Chem. Rev. 24 [1977] 179/275). — [7] D. Kepert (Progr. Inorg. Chem. 25 [1979] 41/144).

#### 1.4 Thermodynamic and Kinetic Stability

Thermodynamic stability in solution is measured by the free-energy change ( $\Delta G$ ) for the overall complexation process, which in turn is related to the enthalpy change ( $\Delta H$ ), the entropy change ( $\Delta S$ ), and the overall formation constant ( $\beta_n$ ) as

$$\Delta G = \Delta H - T\Delta S = -RT \ln \beta_n$$

If the complexation reaction proceeds in steps, each step is described by a similarly equation except that the appropriate stepwise formation constant ( $K$ ) is used. Of these quantities,  $\Delta H$  and either  $\beta$  or  $K$  can be measured experimentally, each by several experimental techniques. Particularly extensive tabulations of  $\lg K$  and  $\lg \beta$  values are available [1, 2].

Comparisons for a given ligand in terms of either  $\Delta G$  or  $\beta_n$  show that complexes of these cations are thermodynamically less stable than those for d-transition metal ions. Comparisons among complexes of the various  $M^{3+}$  ions with particular ligands show no common trend and no single type of variation, although some relationship to variation in crystal or solvated radius might be expected. Depending upon the ligand, three broad trends have been distinguished [3], namely, (1) a more or less regular increase in stability with decreasing crystal radius, (2) increase to essential constancy in the  $Gd^{3+}$ - $Lu^{3+}$  region, and (3) increase to a maximum in the vicinity of the  $Dy^{3+}$  ion. For many, but not all ligands, there exists a discontinuity in  $\lg \beta_n$  or  $\lg K$  at/or in the vicinity of the  $Gd^{3+}$  ion [4]. For a number of ligands, a plot of  $\lg \beta_n$  vs. nuclear charge gives four regular regions of variation separated by discontinuities—the tetrad [5] or double-double [6] effect. Attempted explanations include the inclined W hypothesis [7] and variation in nature of the hydration sphere of the  $M^{3+}$  ion [8].

For complexation in aqueous solution, the entropy change provides the major contribution to stability. This change results in particular from displacement of bonded water molecules by chelating ligands. Changes in hydration numbers are supported by experimental data of various types. By using anhydrous media, the competing effects of water molecules are eliminated, and thermodynamic interpretations are simplified, e.g., by reaction of  $M^{3+}$  ions with ethylenediamine in anhydrous acetonitrile [9].

Complexation, or ligand exchange, reactions in solution have been only incompletely investigated from the kinetic point of view [3]. Those involving simple ligands are usually so rapid that relaxation techniques must be used to follow them. With more complicated ligands, many reactions are slow enough to be investigated by stop-flow or analysis-of-aliquots methods. In aqueous solution, reaction with a ligand by loss of water molecules from the inner hydration sphere may be the rate-determining step. There is good evidence, based upon kinetic data for a number of ligands, that the primary hydration sphere remains the same in the broad  $La^{3+}$ - $Eu^{3+}$  region, that in the  $Eu^{3+}$ - $Ho^{3+}$  region it decreases in size (decrease in coordination number), and that it then remains constant but of smaller size in the  $Ho^{3+}$ - $Lu^{3+}$  region. Fundamentally, however, all ligand exchange processes are relatively rapid.