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der Anorganischen Chemie

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8th Edition

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RARE EARTH ELEMENTS

Part D 3

Coordination Compounds (Continuation)

With 42 illustrations

AUTHORS

Edward R. Birnbaum, Department of Chemistry, New Mexico State University, Las Cruces, New Mexico, USA

John H. Forsberg, Department of Chemistry, Monsanto Hall, Saint Louis University, Saint Louis, Missouri, USA

Yizhak Marcus, Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

FORMULA INDEX

Helga Köttelwesch, Gmelin-Institut, Frankfurt am Main

EDITORS

Therald Moeller, Department of Chemistry, Arizona State University, Tempe, Arizona, USA

Edith Schleitzer-Rust, Gmelin-Institut, Frankfurt am Main

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Preface

Coordination compounds of scandium, yttrium, and the lanthanides are described in series D of the "Rare Earth Elements". Complexes with nitrogen donor and with oxygen donor ligands are described in volumes D 1 and D 2. This volume, volume D 3, continues the discussions of complexes with oxygen donor ligands.

Chapter 1 deals with complexes derived from water. Reference is made to salt hydrates described in volumes of series B and C. Coordination numbers of terpositive rare earth ions toward water molecules in aqueous solutions are discussed in detail in terms of interpretations of physical data.

Chapters 2, 3 and 4 deal successively with the preparation and properties of complexes derived from alcohols and alcoholates, aromatic hydroxy compounds, aldehydes and monoketones. Where Ce^{IV} complexes have been reported for a specific ligand, they are described after the M^{III} complexes. Solution studies are described, when data are available.

Chapter 5 describes complexes with 1,3-diketones and other polyketones. The discovery in 1963 of laser action in rare earth diketonates prompted investigations of their fluorescence spectra and led to isolation and characterization of the first eight-coordinate rare earth complexes. A review of the luminescence properties is presented as an introduction to Chapter 5. Following the initial communication in 1969 several hundred publications have appeared demonstrating the ability of certain tris(diketonato) chelates to act as NMR shift reagents. Since the applications of lanthanide shift reagents are well documented in several extensive review articles, the pertinent sections of this chapter concentrate mainly on the preparation, characterization, and physicochemical properties of the shift reagent adducts, and includes only those NMR studies most closely associated with structural aspects and magnetic properties of the complexes. Chromatographic separation of the rare earths in the gas phase as the volatile, thermally stable tris(dipivaloylmethanato)- and tris(heptafluorodimethyloctanedionato) chelates has been also demonstrated.

Chapter 6 describes complexes with quinones and triphenylmethane dyes. Most of these complexes have been studied in solution, and only a limited number of complexes have been isolated and characterized. The use of triphenylmethane dyes as reagents for the quantitative determination of rare earth ions in solution is well documented.

Chapter 7 covers complexes with ethers and O-heterocycles, including crown ethers, pyranones, derivatives of coumarin, hydroxyflavones, and hematein. Emphasis is substantially on syntheses. Where available, data on crystal and molecular structures and on solution properties are included.

A formula index at the end of this volume lists all ligands and their empirical molecular formulas.

Tempe, Arizona, USA
Frankfurt/Main
December 1980

Therald Moeller
Edith Schleitzer-Rust

Table of Contents

Page

1 Complexes with Water 1

1.1 General 1

1.2 Coordination Numbers of the Aqua Ions 1

1.3 Structure of the Hydrate Coordination Shell 8

1.4 The Rate of Release of Water from the Inner Coordination Shell 9

1.5 The Strength of the Bonding of the Water 11

1.6 The Bonding of the Water Molecules to the Metal Ions 12

2 Alcoholates and Complexes with Alcohols 15

2.1 General Considerations 15

2.2 With Methanol 15

2.3 With Ethanol 18

2.4 With 1-Propanol 20

2.5 With 2-Propanol (= Isopropyl alcohol) 21

2.6 With 1-Butanol 26

2.7 With Isobutyl Alcohol and sec-Butyl Alcohol 27

2.8 With tert-Butyl Alcohol 28

2.9 With 1-Pentanol 28

2.10 With Other Monohydric Alcohols 29

2.11 With 1,2-Ethanediol and Other Alkanediols 31

2.12 With 1,2,3-Propanetriol (= Glycerol) 33

2.13 With Polyols and Sugars 35

3 Salts and Complexes With Aromatic Hydroxy Compounds 37

3.1 With Phenol 37

3.2 With Nitrophenols 37

3.3 — 3.5 With 2-Bromophenol and Nitrophenols 38

3.6 With Dihydroxybenzene and Its Derivatives 39

3.7 With Trihydroxybenzenes and Trihydroxybenzenesulfonic Acid 44

3.8 — 3.10 With 2,3-Dihydroxynaphthalene and Dihydroxynaphthalenesulfonic Acids 45

4 Complexes with Aldehydes and Monoketones 48

4.1 General Aspects 48

4.2 Complexes with Monoketones and Benzaldehyde 48

4.3 Complexes with Hydroxyaldehydes and Hydroxyketones 49

4.3.1 With Salicylaldehyde 49

4.3.2 With Derivatives of Salicylaldehyde 51

Page
4.3.3 With 3-Hydroxybenzaldehyde . . . 51
4.3.4 With 2,4- and 3,4-Dihydroxybenzaldehyde . . . 51
4.3.5 With 2-Hydroxy-1-naphthaldehyde . . . 52
4.3.6 — 4.3.8 With Hydroxyderivatives of Acetophenone . . . 52
4.3.9 With 2-Hydroxybenzophenone . . . 53
4.3.10 With Tropolone . . . 54
  $M(C_7H_5O_2)_n^{3-n}$ Complexes. Formation in Solution . . . 54
  Tris Chelates . . . 55
  Mixed Complex Derived from Tropolone and 1,10-Phenanthroline . . . 58
  Tetrakis Chelates . . . 58
    Hydrogen Compound $H[M(C_7H_5O_2)_4]$ . . . 58
    Alkali Metal Salts $M'[M(C_7H_5O_2)_4]$ . . . 60
    Cerium(IV) Compound $Ce(C_7H_5O_2)_4$ . . . 61
With Derivatives of Tropolone . . . 61

5 Complexes with Diketones and Polyketones . . . 65

5.1 Complexes with 1,3-Diketones . . . 65
General Literature . . . 65
5.1.1 General Aspects. Luminescence Studies . . . 65
5.1.2 Complexes with Acetylacetone . . . 76
  $M(acac)_n^{3-n}$. Formation and Properties in Solution . . . 76
  Tris(acetylacetonato) Compounds . . . 82
    $M(acac)_3$ . . . 82
    $M(acac)_3 \cdot n H_2O$ . . . 85
      Preparation and Stability . . . 85
      Crystal and Molecular Structures . . . 85
      Spectral Studies . . . 89
  Adducts of Tris(acetylacetonato) Compounds . . . 95
    Solvates $M(acac)_3 \cdot n H_2O \cdot mS$ . . . 95
    Complexes with Bidentate Organic Bases . . . 96
    Complexes with 4-Amino-3-penten-2-one . . . 98
    Complex with Diantipyrylmethane . . . 99
    Complexes with Tributyl Phosphate, Trioctylphosphine Oxide and Triphenylphosphine Oxide . . . 99
  Tetrakis(acetylacetonato) Compounds of the Type $M'[M(acac)_4]$ . . . 99
  Cerium(IV) Compound $Ce(acac)_4$ . . . 100
  Other Acetylacetonato Complexes . . . 102
5.1.3 Complexes with 1,1,1-Trifluoro-2,4-pentanedione . . . 102
  Lewis Base Adducts of the Tris Chelates . . . 103
  Tetrakis Chelates of the Type $M'[M(C_5H_4F_3O_2)_4]$ . . . 104
  Cerium(IV) Compound $Ce(C_5H_4O_2F_3)_4$ . . . 105
5.1.4 Complexes with 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione . . . 105
  Tris Chelates $M(C_5HF_6O_2)_3 \cdot n H_2O$ . . . 105
  Lewis Base Adducts of the Tris Chelates . . . 108
  Tetrakis Chelates of the Type $M'[M(C_5HF_6O_2)_4]$ . . . 109
    Alkali Metal Salts . . . 109
    Ammonium Salts . . . 111
    Alkylammonium Salts . . . 111
    Pyridinium Salts . . . 112
    Salts of Pyridinium Derivatives . . . 113
    Piperidinium Salts . . . 113
    Piperazinium Salt and Other Salts . . . 114

Page

Cerium(IV) Compound $Ce(C_5HF_6O_2)_4$ 114
Pentakis Chelates 114
Complexes Derived from Hexafluoroacetylacetonate and Trifluoroacetate Ions 115

5.1.5 With 3-(2,4,6-Trimethylphenyl)-2,4-pentanedione (= 3-Mesitylacetylacetone) 116

5.1.6 Complexes with 2,4-Hexanedione 116
$M(C_6H_9O_2)_n^{3-n}$ Complexes. Formation in Solution 116
Isolated Compounds 116
Complexes Derived from 2,4-Hexanedione and Other Ligands 117

5.1.7 Complexes with Derivatives of 2,4-Hexanedione 119

5.1.8 Complexes with Derivatives of 2,4-Heptanedione 122

5.1.9 Complexes with 3,5-Heptanedione and its Derivatives 124
With 3,5-Heptanedione, Monomethyl- and Dimethyl-3,5-heptanediones 124
With 2,2,6-Trimethyl-3,5-heptanedione 124
With 2,2,6,6-Tetramethyl-3,5-heptanedione (= Dipivaloylmethane) 125
  $M(C_{11}H_{19}O_2)_n^{3-n}$ Complexes. Formation in Solution 125
  Tris Chelates $M(C_{11}H_{19}O_2)_3 \cdot nH_2O$ (n = 0, 1) 125
    Preparation 125
    Crystallographic Properties 125
    Magnetic Properties 130
    Optical Properties 131
    Thermal Stability 132
    Mass Spectra and Photochemical Reactions 133
  Lewis Base Adducts of the Tris Chelates 136
  $M(C_{11}H_{19}O_2)_3 \cdot B$. Formation Constants 136
  Isolated Adducts 136
    With Pyridine 136
    With 3-Methylpyridine 141
    With 4-Methylpyridine 142
    With 3,5-Dimethylpyridine 145
    With 1,4-Diazine 146
    With 1-Azabicyclo [2.2.2]octane (= Quinuclidine) 146
    With 2,2'-Bipyridine and 1,10-Phenanthroline 147
    With 1,8-Naphthyridine 148
    With Phthalazine 149
    With Dimethylformamide 149
    With Other Lewis Bases 151
  Tetrakis Chelates 153
  Other Complexes with 2,2,6,6-Tetramethyl-3,5-heptanedione 154

5.1.10 Complexes with 6,6,7,7,8,8,8-Heptafluoro-2,2-dimethyl-3,5-octanedione 155
$M(fod)_n^{3-n}$. Formation in Solution 155
Lewis Base Adducts of the Tris Chelates 158

5.1.11 Complexes with Other Aliphatic Diketones 164

5.1.12 Complexes with 1-Phenyl-1,3-butanedione 165
$M(C_{10}H_9O_2)_n^{3-n}$ Complexes. Formation in Solution 165
Tris Chelates 166
  $M(C_{10}H_9O_2)_3$ 166
  $M(C_{10}H_9O_2)_3 \cdot nH_2O$ 167
Adducts of the Tris(benzoylacetonato) Complexes 171
Tetrakis Chelates of the Type $M'[M(C_{10}H_9O_2)_4]$ 174
  Alkali Metal Salts 174
  Piperidinium Salts 175

Page

    Alkylammonium Salts 178
    Morpholinium Salt 178
  Cerium (IV) Compound Ce$(C_{10}H_9O_2)_4$ 178
  Other Benzoylacetonato Complexes 180

5.1.13 Complexes with 4,4,4-Trifluoro-1-phenyl-1,3-butanedione (= Benzoyltrifluoroacetone) 181
  Tris Chelates M$(C_{10}H_6F_3O_2)_3 \cdot n\,H_2O$ 181
  Lewis Base Adducts of the Tris Chelates 182
  Tetrakis Chelates of the Type M'[M$(C_{10}H_6F_3O_2)_4$] 183
  Cerium (IV) Compound Ce$(C_{10}H_6F_3O_2)_4$ 187

5.1.14 Complexes with Aryl-substituted β-Diketones ArC(O)CH$_2$C(O)R (= HL) 188
  M$(L)_n^{3-n}$. Formation in Solution 188
  Isolated Tris Chelates 189
  Tetrakis Chelates 190

5.1.15 With 1,3-Diphenyl-1,3-propanedione (= Dibenzoylmethane) 192
  M$(C_{15}H_{11}O_2)_n^{3-n}$ Complexes. Formation in Solution 192
  Tris Chelates 192
    Anhydrous Compounds M$(C_{15}H_{11}O_2)_3$ 192
    Hydrates M$(C_{15}H_{11}O_2)_3 \cdot n\,H_2O$ 194
    Lewis Base Adducts of the Tris Chelates 196
  Tetrakis Chelates of Type M'[M$(C_5H_{11}O_2)_4$] 200
    Alkali Metal Salts 200
    Ammonium and Alkylammonium Salts 200
    Pyridinium and Piperidinium Salts 203
    Other Salts 206
  Cerium (IV) Compound Ce$(C_{15}H_{11}O_2)_4$ 206
  Other Dibenzoylmethanato Complexes 207

5.1.16 Complexes with Derivatives of 1,3-Diphenyl-1,3-propanedione 210

5.1.17 Complexes with 1,3-Di(1-naphthyl) and 1,3-Di(2-naphthyl)-1,3-propanedione 214

5.1.18 Complexes with Curcumin 214

5.1.19 Complexes with 1,3-Bis(4-pyridyl)-1,3-propanedione 215

5.1.20 Complexes with Furylderivatives of 1,3-Propanedione and 1,3-Butanedione 215

5.1.21 With 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione 217
  Tris Chelates M$(C_8H_4F_3O_2S)_3 \cdot n\,H_2O$ 218
  Lewis Base Adducts of the Tris Chelates 220
    With Nitrogen Donor Ligands 220
    With Oxygen Donors 223
  Tetrakis Chelates of Type M'[M$(C_8H_4F_3O_2S)_4$] 227
  Cerium (IV) Compound Ce$(C_8H_4F_3O_2S)_4$ 232
  Mixed Complexes Derived from Thenoyltrifluoroacetone and Other Ligands 232

5.1.22 Complexes with Other Thienyl Derivatives of 1,3-Diketones 235

5.1.23 Complexes with Selenophenyl Derivatives of 1,3-Diketones 236

5.1.24 With Formyl- and Oxoalkyl Derivatives of Cyclohexanone 238

5.1.25 With 5,5-Dimethyl-1,3-cyclohexanedione 239

5.1.26 Complexes with Optically Active β-Diketones 240
  With 3-Trifluoroacetyl-*d*-camphor 240
    Tris Chelates M$(C_{12}H_{14}F_3O_2) \cdot n\,H_2O$ 240
    Lewis Base Adducts of the Tris Chelates 241
  With Other Derivatives of Camphor 242

Page

5.2 Complexes with Other Diketones and Polyketones . . . 247
5.2.1 With Tribenzoylmethane . . . 247
5.2.2 With 2-Acetyl-1,3-indandione . . . 248
5.2.3 With Squaric Acid . . . 248
5.2.4 With 3-Hydroxy-4-methyl-3-cyclobutene-1,2-dione . . . 250
5.2.5 Croconic Acid . . . 250
5.2.6 With Rhodizonic Acid . . . 251

6 Complexes with Quinones . . . 352
6.1 With Semiquinone Radical Anions . . . 252
6.2 With Derivatives of 1,2-Benzoquinone . . . 252
6.3 With Derivatives of 1,4-Naphthoquinone . . . 253
6.4 With Derivatives of Anthraquinone . . . 254
6.5 Complexes with Triphenylmethane Dyes and Analogous Compounds . . . 257
6.5.1 With Aluminon . . . 257
6.5.2 With Eriochrome Azurol B . . . 258
6.5.3 With Chromal Blue G . . . 258
6.5.4 With Pyrocatechol Violet . . . 259
6.5.5 With Eriochrome Cyanine R (= Solochrome Cyanine R) . . . 259
6.5.6 With Chrome Azurol S . . . 260
6.5.7 Complexes with Phthalexon S . . . 261
6.5.8 With Xylenol Orange . . . 262
6.5.9 With Glycinecresol Red . . . 264
6.5.10 With para-Xylenolphthalexon S . . . 265
6.5.11 With Methylthymol Blue . . . 265
6.5.12 With Glycinethymol Blue . . . 268
6.5.13 With Fluorescein and Its Derivatives . . . 268
6.5.14 With 2-Hydroxyphenylfluorone . . . 269
6.5.15 With Pyrogallol Red and Bromopyrogallol Red . . . 270

7 Complexes with Ethers and O-Heterocycles . . . 271
7.1 With Diethyl Ether . . . 271
7.2 With 1,2-Diethoxyethane . . . 271
7.3 With Tetrahydrofuran . . . 271
7.4 With Dioxane . . . 273
7.5 Complexes with Macrocyclic Ethers . . . 275
7.5.1 With Crown Ethers . . . 275
  With 12-Crown-4 . . . 275
  With 15-Crown-5 . . . 276
  With 18-Crown-6 . . . 277
  With Dicyclohexyl-18-crown-6 . . . 278
  With Benzo-15-crown-5 . . . 280
  With Dibenzo-18-crown-6 . . . 283
  With Dibenzo-30-crown-10 . . . 285

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Page

7.6 Complexes with Furanone Derivatives . . . 286
7.6.1 With Ascorbic Acid . . . 286

7.7 Complexes with Pyranone Derivatives . . . 287
7.7.1 With Dehydroacetic Acid . . . 287
7.7.2 With 2,6-Dimethyl-4-pyrone . . . 287
7.7.3 With 3-Hydroxy-2-methyl-4-pyrone . . . 290
7.7.4 With Kojic Acid . . . 291
7.7.5 With Chlorokojic Acid . . . 294

7.8 Complexes with Derivatives of Coumarin . . . 294

7.9 Complexes with Hydroxyflavones . . . 296

7.10 Complex with Hematein . . . 297

Ligand Formula Index . . . 298

Table of Conversion Factors . . . 323

1 Complexes with Water

Y. Marcus
Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem
Jerusalem, Israel

1.1 General

Much of the earlier work concerning the coordination of water with Sc, Y, and the lanthanide ions in solution has been rather speculative, the speculations resting on the coordination of water to the metal ion in crystalline compounds. Moeller et al. [1] summarize this phase of the work, stating that the compositions of coordination compounds (solid and in solution) were consistent with the assignment of the coordination number six to Y and the rare earth metal ions. Although this coordination number has been assumed by many authors, there was an increasingly impressive array of evidence that the true coordination number was larger than six [1, 2].

The evidence for coordination numbers for water > 6 includes the structures of the crystalline salt hydrates $M(BrO_3)_3 \cdot 9H_2O$ [3] and $M(C_2H_5OSO_3)_3 \cdot 9H_2O$ [4], which form isomorphous enneahydrate crystals along the whole series of the rare earths (M = La to Lu) [5 to 9] each with all nine water molecules coordinated to the metal ion. It includes also, however, structures such as $MCl_3 \cdot 7H_2O$ (M = La to Pr) and $MCl_3 \cdot 6H_2O$ (M = Nd to Lu) [10 to 14], $M(NO_3)_3 \cdot 6H_2O$ (M = La to Lu) [15], and $M_2(SO_4)_3 \cdot 9H_2O$ (M = La to Pr) and $M_2(SO_4)_3 \cdot 8H_2O$ (M = Nd to Lu) [16 to 18], where only a part of the coordination shell is made up of the oxygen atoms of the water molecules, while the rest is made up of chlorine atoms or oxygen atoms from the anions. The structures of these and other crystal hydrates are discussed in detail in the Gmelin Handbook (Sc, Y, La to Lu), see "Seltenerdelemente" Volumes C 2, 1974 (the nitrates), C 4 (the chlorides, to be published), C 6, 1978 (the bromates), and C 8, 1981 (the sulfates and ethylsulfates), and will not be treated here. The structure [3] of the inner coordination shell of crystalline $Nd(BrO_3)_3 \cdot 9H_2O$, i.e., that of $Nd(H_2O)_9^{3+}$, is shown in Fig. 1-2, p. 8, for reference purposes only.

This chapter discusses the aqua-complexes formed in solution from the following aspects: (a) the coordination number, i.e., the primary hydration number, of the ions Sc^{3+}, Y^{3+}, and the lanthanides La^{3+} to Lu^{3+}; (b) the structures of these hydrated ions; (c) the rate at which H_2O is released from the hydration shell, as a measure of the tightness of its binding; (d) some comments on the thermodynamic data for the Gibbs free energy, enthalpy, and entropy of hydration, as a measure of the strength of the coordination of the water; (e) some comments on the bonding of the water to the metal ions.

1.2 Coordination Numbers of the Aqua-Ions

Hydration numbers are definable only operationally, i.e., by the method according to which they are determined. Consequently, they are generally more sensitive to the method of determination than to the ion, the hydration of which they should describe. Fortunately, however, the first hydration shell can be described rather definitely by the requirement, that the oxygen atoms of the water molecules be in direct contact with the metal ion. Hence so called "primary hydration numbers" are more or less well defined descriptors of the number of water molecules in the first coordination shell of the metal ions in dilute aqueous solutions, devoid of coordinating ligands other than water. In the following, "primary hydration number" will be taken as synonymous with "coordination number" in such dilute aqueous solutions.

For some time a controversy raged, concerning the question, whether the coordination number stays constant or changes, abruptly or over few neighboring elements, as the atomic number Z varies from 57 (La) to 71 (Lu). The suggestion that the primary hydration number changes from a higher one (presumably 9) for La^{3+}, Ce^{3+}, Pr^{3+}, and Nd^{3+} to a lower one (presumably 8) for Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+} has been made in a number of papers, amongst the first ones and the most influential of which being that of Spedding et al. [19]. However, other authors [20 to 25] concluded that their data could very well be interpreted with, or even required for their interpretation, a constant primary hydration number along the series. These suggestions and conclusions were all based on indirect evidence, and must yield to recent results from more nearly direct determinations.

1.2.1 Data from X-Ray Scattering

The most direct values of primary hydration numbers are available from the analysis of atomic radial distribution functions (ARDF's), obtained from low angle X-ray diffraction by aqueous solutions of the rare earth metal halides. The results obtained to date by this method are summarized in Table 1/1.

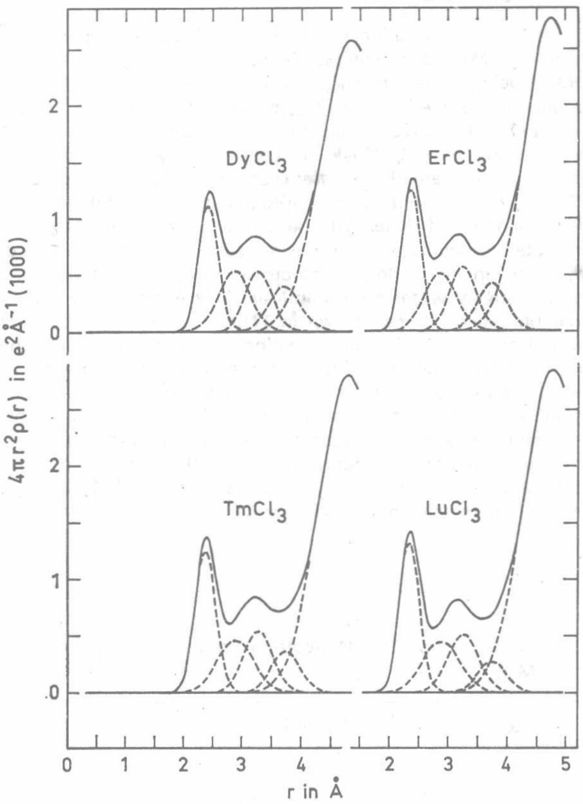
Table 1/1

Information Obtained from the First and Some of the Subsequent Peaks in the ARDF's of Rare Earth Halides in Aqueous Solutions.

salt	concentration mol/kg H_2O	first peak coord. No.	first peak d_{M-O}, in Å	peak for M-X d_{M-X}, in Å	Ref.
$LaCl_3$	1.74, 2.10, 2.67	8.0	2.48	4.7	[26, 27]
	2.0, 3.81	9.13	2.58	5.00	[28]
$LaBr_3$	2.66	8.0	2.48	4.8	[29]
$PrCl_3$	3.80	9.22	2.54	4.97	[28]
$NdCl_3$	0.56, 0.85, 1.73	8.0	2.41	4.9	[30, 31]
	3.37	8.90	2.51	4.89	[28]
$SmCl_3$	1.43	9.9	2.42	4.5	[32]
$GdCl_3$	0.85, 2.66	8.0	2.37	4.8	[31, 33]
	1.43	9.9	2.40	4.5	[32]
$TbCl_3$	3.49	8.18	2.41	4.82	[34]
$DyCl_3$	3.29	7.93	2.40	4.85	[34]
$ErCl_3$	3.54	8.19	2.37	4.79	[34]
	0.95, 1.37, 3.05	6.5	2.3	4.6	[35]
ErI_3	1.33	6.3	2.3	5.2	[35]
$TmCl_3$	3.63	8.12	2.36	4.79	[34]
$LuCl_3$	3.61	7.97	2.34	4.78	[34]

The ARDF is $4\pi r^2\rho(r)$, where r is the distance from a given (metal) atom and $\rho(r)$ the density of atoms at the distance r (**Fig. 1-1**). Its units are $e^2/Å$ (e is an electron). The area under the curve from suitably chosen r_1 to r_2, divided by the area (in e^2) expected per single neighbor, is the number of nearest neighbors of the atom at the origin. The starting distance, r_1 may be taken as zero, or as the distance where $\rho(r)$ starts practically to differ from zero. The determination of the final distance, r_2, is rather a matter of judgement, and the accuracy of the coordination number depends heavily on its proper choice. It is unfortunate that the results published by various authors do not agree. Thus the ARDF for aqueous $ErCl_3$, published already in 1960 [35] by Brady, differs in the positions and the shapes of the peaks from that given by Habenschuss, Spedding in 1979 [34], and the ARDF for aqueous $LaCl_3$ of Smith, Wertz [26] differs in these respects from the one of Habenschuss, Spedding [28].

Fig. 1-1



Atomic radial distribution functions of aqueous Dy, Er, Tm, and Lu chlorides [34]. The dashed curves represent the resolution of the experimental curve into 5 Gaussian components.

The work of Brady [35] is now superceded. (Brady himself considered that rather than his direct result of 6.5 for the first coordination shell, "within the experimental error the number is six". The distance to the first peak is given with only one significant decimal figure, rather than the two or three given in the later studies.) A coordination number of eight (8.1 ± 0.1) as a mean for five elements for the heavy rare earth aquo-complexes seems to be well established by the painstaking work of Habenschuss, Spedding [34]. With this agrees also the coordination number of eight (8.0 ± 0.2) given by Steele, Wertz [31, 33] for Gd^{3+}, but not the discordant result 9.9 given by Ryss et al. [32] for this ion, as well as for Sm^{3+}. A real discrepancy is noted for the light rare earth metal ions, where Habenschuss, Spedding [28] give a coordination number of nine (9.1 ± 0.1 as a mean for three elements), whereas Wertz et al. [26, 27, 29 to 31] report a coordination number of eight.

No dependence on the anion was discerned in those studies where two different salts of a given metal were compared (aqueous $LaCl_3$ [26, 27] and $LaBr_3$ [29], aqueous $ErCl_3$ and ErI_3 [35]). Comparative data obtained and interpreted in the same way by the same author should be valid, in this respect, even if the quantitative conclusion is in error, as it evidently is for the results with Er^{3+}.

1.2.2 Data from NMR Peak Areas

Another way to obtain primary hydration numbers in a direct manner is the evaluation of the peak areas obtained in proton NMR measurements. These are made on solutions in a mixed aqueous organic solvent, capable of being cooled to such a low temperature that a peak corresponding to the bound water molecules is observed [36 to 38], separate from that for bulk water. A suitable solvent is deuterated acetone, d^6-CH_3COCH_3, capable of being cooled down to −100°C (and down to −120°C when mixed with Freon −12, CCl_2F_2, if it is necessary to lower the temperature further) in order to slow down the exchange rate of the water (see section 1.4, p. 9) sufficiently for a separate peak to be observed. The acetone is said not to coordinate to the metal ion in these solutions in the presence of a sufficient amount of water, but the low dielectric constant in these solutions and the low temperature promote ion pairing. Nitrate ions are known to enter the first coordination shell of the lanthanides, and no convincing evidence was presented in these studies that perchlorate ions do not do so too, in the relatively water-poor solutions. This explains the low primary hydration numbers obtained in perchlorate solutions, shown in Table 1/2. Another explanation [37] is that only some of the water molecules in the first coordination shell exchange sufficiently slowly to give a separate peak, whereas the others, still in the first coordination shell but bound a bit more loosely, exchange too rapidly, and are included with the signal for the bulk water. Inspection of Fig. 1-2 shows that in the crystalline enneahydrate six water molecules are equivalent, but differ from the other three. That inner-sphere ion association decreases the primary hydration numbers appreciably, under the conditions of the experiments, is demonstrated by the results for nitrate salts, or where nitric acid was added to the perchlorate salts [36 to 38]. The hydration numbers recorded in Table 1/2, even for the perchlorate salts, must therefore be considered as lower limits.

Table 1/2

Hydration Numbers Observed at <−95°C in d^6-Acetone Containing Some Water[a] by Proton NMR.

cation	perchlorate	nitrate
Sc^{3+}	[b],[c]	3.7 to 4.1 [36]
Y^{3+}	[c]	2.2 to 2.6 [36]
La^{3+}	6.0 to 6.4 [37]	
Ce^{3+}	4.5 to 5.5 [37]	
Pr^{3+}	≈6 [38]	
Nd^{3+}	≈6 [38]	
Tb^{3+}		≈2 [38]
Dy^{3+}		≈3 [38]
Ho^{3+}	≈3 [38]	
Er^{3+}	4.2 to 6.4 [38]	1 to 2 [37, 38]
Tm^{3+}		≈2 [38]
Yb^{3+}	3.6 to 4.2[d] [38]	1.6 to 2.0 [38]
Lu^{3+}	5.8 to 6.1 [38]	2.2[d] [38]

[a] Unless otherwise stated, mole ratio of water to metal ion in solution is (6 to 15) : 1.—[b] No separate signals for bound and bulk water observable down to −100°C [39].—[c] In the presence of 1M $HClO_4$ additional to the metal nitrate, hydration numbers of 5.1 for Sc^{3+} and ≈2.4 for Y^{3+} are observed [39].—[d] In the presence of a large excess of water (>50 times the metal ion concentration), the hydration number 8 is observed for Yb^{3+} [40] and 6 for Lu^{3+} [108].

1.2.3 Data from Compressibilities

Another method, that is purported by its users to give primary hydration numbers, is the compressibility method. According to Passinsky [41] the central ion with the primary water of hydration are incompressible, because of the strong electrical field of the ion. The large pressure exerted by this field is greater than the limit of ca. 6.8×10^8 Pa, above which water is practically no longer compressible [42]. The electrostriction caused by this field-induced pressure produces thus an incompressible hydrated core, and the number of water molecules affected in this way per ion is identified with its primary hydration number. This is given as $h^\infty = -\varnothing_{\varkappa}^{\infty}/\varkappa^\circ_{H_2O}V^\circ_{H_2O}$, where $\varnothing_{\varkappa}^{\infty}$ is the apparent molar isothermal compressibility, extrapolated to infinite dilution, and $\varkappa^\circ_{H_2O}$ and $V^\circ_{H_2O}$ are the compressibility and molar volume of pure water [43]. Experimental data on compressibilities pertain to electrolytes rather than to ions, but are additive with respect to ionic contributions at infinite dilution. If the contribution of one ion is fixed arbitrarily, those of the others are obtained [43]. The compressibilities involved should be the isothermal ones, but adiabatic compressibilities, obtained from ultrasound velocities, are used in their stead, if not all the data required for the conversion (expansibilities, molar volumes and heat capacities) are available [44 to 48]. The results from several authors are shown in Table 1/3. No cognizance of the hydration of the anions is made in the work of Jezowska-Trzebiatowska et al. [44 to 47] so that the hydration number obtained for the whole electrolyte is ascribed to the rare earth metal cation only. However, the differences between chloride, nitrate, and perchlorate data [46] show the effect of the anion. According to Padova's calculation [49] from the compressibility data of Spedding, Atkinson [50], ca. 2.7 should be subtracted for each chloride ion and ca. 1.3 for each nitrate ion from the hydration number of the salt, to give that for the metal ion, recorded in Table 1/3 in the column marked – [43, 49]. Janenas [42] proposed a method differing somewhat from Passinsky's [41, 43], and obtained with it hydration numbers larger by 4 to 5 units. The fluctuations in the hydration numbers reported by Voleisiene et al. [48] have not been explained. In general, it is seen that the primary hydration numbers obtained from the compressibilities are larger than the coordination numbers obtained from the ARDF's, and should represent upper limits. A slight trend of these hydration numbers to increase with Z, the atomic number of the elements, can be discerned. Apparently these hydration numbers comprise some of the secondary solvation, which may, indeed, increase as the size of the metal ions decreases with increasing Z, and the strength of the electrical field around them increases.

Table 1/3

Primary Hydration Numbers Obtained from Compressibilities.

cation	anions and references								
	ClO_4^-	ClO_4^-	Cl^-	NO_3^-	ClO_4^-	NO_3^-	NO_3	–	NO_3^-
	[44]	[45]	[46]	[46]	[46]	[47]	[42]	[43, 49]	[48]
Y^{3+}							15.59		
La^{3+}	12.7					10.4	12.75	11	11.6
Ce^{3+}						*)	12.36	13	15.6
Pr^{3+}	12.9		15.7	10.1	12.0	10.1			9.1
Nd^{3+}	12.5		17.1	10.9	12.8	10.9		12	8.8
Sm^{3+}	11.05					12.0			16.8
Eu^{3+}	10.45		*)	*)	*)	*)			
Gd^{3+}	11.0					12.0			9.5
Tb^{3+}	11.7	11.74				13.0			
Dy^{3+}	11.95	12.01				12.8			17.5
Ho^{3+}	12.5	12.71				12.8			
Er^{3+}	12.6	12.39				12.2		12	16.4
Tm^{3+}	12.8	12.93				*)			
Yb^{3+}	13.0	12.98						13	

*) Compressibilities varied with concentration in a manner that precluded the calculation of hydration numbers.

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