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THE COORDINATION CHEMISTRY OF YTTRIUM AND THE RARE EARTH METAL IONS

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I. INTRODUCTION

Classically, the coordination chemistry of yttrium and the rare earth metal ions was of interest only as it pertained to the separation of these ions from each other. More recently, however, interest in other aspects of this chemistry has developed, paralleling the substantial increase in investigative effort and theoretical interpretation in the area of coordination compounds in general. Although certain topics have been discussed in earlier reviews (360, 361), it is reasonable both to expand upon and update this information and to introduce additional topics that are pertinent to an over-all understanding of the general subject. Accordingly, such fundamental items as the characteristics of known complex species, both in the solid state and in solution, the factors that are involved in the formation of these species, and the nature of the ligand-cation bond are considered. These topics are then discussed in terms of uses to which the complex species are put. Finally, it is shown that the related coordination chem-

istry of scandium and the actinide metal ions is readily understandable in terms of differences from and similarities to the coordination chemistry of the rare earth metal ions.

The coordination chemistry of the rare earth metal ions can, with profit, be contrasted and compared with that of the d-type transition metal ions. A striking conclusion is that the area is much more limited. Appreciably stable complex species, other than the hydrated cations themselves, are obtained only when the most strongly chelating ligands are used and, in particular, when these ligands contain highly electronegative donor atoms (*e.g.*, oxygen). Both the electronic configuration of the cation and its radius are of importance in arriving at an understanding of both this phenomenon and the paucity of rare earth metal ion complexes in general.

The significance of electronic configuration follows from the following considerations. The stabilities of coordination compounds of the d-type transition metal

ions are related to participation of the d electrons in the metal-ligand bond through hybridization of metal electronic orbitals and overlap of these hybrid orbitals with appropriate ligand orbitals. The rare earth metal ions differ from each other in the number of electrons in the 4f orbitals, which orbitals are effectively shielded from interaction with ligand orbitals by electrons in the 5s and 5p orbitals. If hybridization is to occur, it must of necessity involve normally unoccupied higher-energy orbitals (*e.g.*, 5d, 6s, 6p), and hybridization of this type can be expected only with the most strongly coordinating ligands. Significant cation-ligand attractions are thus largely electrostatic in character, and the complex species formed by these cations compare more closely with those derived from the calcium, strontium, and barium ions than with those derived from the d-type transition metal ions (267, 361, 486). These cations (d^0 , with rare gas cores) are thus of the A-type (486).

Under these circumstances, both cation size and differences in the sizes of the several cations are of importance. The rare earth metal ions, in any state of oxidation, are large by comparison with cations that give the most stable complexes, and the change in size with increasing atomic number (lanthanide contraction) is not substantial (361). Strong electrostatic attractions between rare earth metal ions and ligands will, therefore, be limited in number, but they will increase in magnitude from cation to cation for a given oxidation state as cation radius decreases, and for a given metal as cation charge increases. The relatively small over-all stabilities of most of the known complex species, the generalized increase in stability with decreasing size of tripositive cation for species containing a common ligand, and the increase in stability for a given ligand with cation charge in those few cases where this is possible (*e.g.*, Ce^{+3} to Ce^{+4} , Eu^{+2} to Eu^{+3}), as delineated in subsequent sections of this review, all confirm these general considerations.

The absence of significant interactions between ligand and 4f orbitals is supported by observations that complexing groups have only small effects upon the magnitudes of the permanent magnetic moments of the tripositive ions (161, 162, 225, 233, 234, 242, 368) or upon the positions of their sharply defined, characteristic absorption bands in the ultraviolet and visible regions (59, 135-141, 156, 226-229, 363, 368, 377, 385, 462, 581, 600). Indirectly, this is evidence for the ionic model, as is also the absence of π -bonding interactions in the cyclopentadiene derivatives of these ions (47, 331, 625). On the other hand, the possibility of covalent interactions cannot be completely excluded (267). For descriptive purposes, covalency is often assumed when a compound fails to show in solution the chemical reactions of its contained cation when it dissolves in nonpolar solvents, or when, if potential asymmetry exists, it is resolvable into optically active enantiomers.

Although none of these behaviors is an absolute criterion of covalency, each is satisfied by at least the acetylacetonate chelates (346, 367, 377, 581). There is also evidence based upon nephelauxetic effects of some degree of covalency in some of the complex species (266, 267).

The literature coverage in this review is essentially complete through 1962. Only a few references to papers appearing subsequently have been included.

II. SURVEY OF COMPLEX SPECIES

Even though many factors appear to militate against their formation, a number of complex species derived from yttrium and the rare earth metal ions have been described. Some of these species exist only in solution and do not have sufficient stability to be carried through series of reactions without undergoing dissociation into their components. Others exist only in the solid state and dissociate or decompose upon dissolution. Still others have sufficient stability with respect to their components that they exist both in solution and in the solid state and thus appear capable of participating in reactions without undergoing change in composition. The majority of the species that have been characterized are derived from the tripositive metal ions. Of the tetrapositive metal ions, only cerium(IV) gives coordination entities that resist reduction in aqueous systems. Species containing other tetrapositive metals are obtainable only as solids. A limited number of entities containing the dipositive metal ions resist oxidation sufficiently to exist in aqueous solution, but no solid dipositive compounds have yet been described. A notably small amount of information is available on complex formation in nonaqueous systems.

A. CLASSIFICATION OF COMPLEX SPECIES

A broad classification, based upon these points and derived in part from those previously published (360, 361), is given in Table I. Although this classification is arbitrary, in the sense that it cannot avoid completely overlapping among the properties of all species, and incomplete, in the sense that only representative examples are included, it does provide a framework for more detailed discussion.

1. Ion-Pair Associations

Although yttrium and the rare earth metal ions form a number of series of double salts, it is probable that the majority of these salts can be characterized only in the solid state and thus owe their existence more to the requirements of crystal symmetry than to those of complex formation. On the other hand, the existence of ion-pair associations that are limited to aqueous solutions and are probably not continued in the solid com-

pounds isolated from such solutions can be demonstrated experimentally by a number of measurements. Included among these measurements are variations, in the presence of certain anions, in the polarographic reduction of europium(III) (224), in the distribution of the cations between solution and an ion-exchange resin (94, 167, 354, 355), in the distribution of species between aqueous and nonaqueous phases (88, 93, 153, 407, 427), in transference number and conductance (109, 116, 526), in solubilities (21, 98, 99), and in potentiometric data (172, 417, 491, 518). Many of these measurements give both compositions (Table I) and stabilities (Tables II and III) of the complex species. Spectrophotometric measurements involving alteration in the intensities or wave lengths of the characteristic absorption bands resulting from "forbidden" 4f transitions indicate the presence of ion-pair associations (59) but have limited application to the evaluation of their stabilities (59, 303). Spectrophotometric measurements involving new absorption bands characteristic of the ion-pair association provide data of both types (212). The ion-pair association complexes formed by yttrium and the rare earth metal ions are comparable with those formed by other cations (388). Although but few cerium(IV) species have been described, these entities should be more characteristic than the corresponding cerium(III) species as a consequence of the enhanced cationic charge.

2. Isolable Adducts

In compounds of this type, some or all of the molecules of water of hydration have been replaced by other donor species. The strengths of the cation-water bonds are such that reported adducts both involve relatively few donors and quite generally revert to the hydrated cations upon dissolution in water. Certain of these compounds, notably those containing thiourea (477), urotropine (115, 117), antipyrine (117, 262, 338, 340, 472, 623), and pyramidone (472), have sufficient crystal stability to permit their crystallization from aqueous solutions. Others, notably the ammine and amine adducts (135, 453, 612), must be prepared under anhydrous conditions, whereas still others, in particular the dioxane adducts (590), are formed by reaction of the donor with the crystalline hydrates. The tributyl phosphate compounds (496) also appear in the nonaqueous phase resulting from the solvent extraction of aqueous systems (419, 420, 483).

3. Chelates

Chelated species containing yttrium and the rare earth metal ions are more numerous than all other complex species. This fact is undoubtedly a consequence of the general observation that chelation invariably leads to greater stability with respect to dissocia-

tion to the component species than does complex formation by the same donor atoms in nonchelated structures. Similarly, those ligands that can give simultaneously more than a single metal-chelate ring [notably the polyaminepolycarboxylates (8, 67, 198, 203, 287, 328, 363-365, 368, 369, 372, 375, 455, 567, 569, 570)] involving a given metal ion form the most stable and probably the best characterized species. Although most of the known chelates contain, of course, the tripositive ions, a significant number are derived from europium(II) and cerium(IV), the two nontriple positive ions that are most stable in aqueous solution. Many of the species listed in Table I have been studied only in aqueous solution, and almost exclusively in terms of formation constants (Tables II and III). It is not known that solid compounds containing these ionic species can be isolated in all instances, but the successful isolation of a number of solid chelates (19, 40, 67, 175, 177, 185, 257, 287, 262, 363, 368, 372, 441, 451, 460, 474, 581, 627) suggests that the same can be effected in many other instances.

The chelated species include both inner complexes and ions. Typical examples of the first class are those derived from the 8-quinolinols and the 1,3-diketones. Greenish to yellow water-insoluble compounds of the apparent composition $\text{Ln}(\text{on})_3$ have been obtained by precipitation from buffered aqueous solutions (40), but more detailed study has shown that only in isolated cases, and there perhaps only as a result of coincidence, do compounds of this exact stoichiometry result (257). Basic precipitates containing less than this theoretical quantity of 8-quinolinol are commonly obtained. The 3:1 stoichiometry is more closely approximated in the less soluble 5,7-dihalo-8-quinolinol derivatives (257). It is not known with certainty that definite hydrates do not exist. In chloroform solution, these chelates show major light absorptions characteristic of the quinolinol structure below 4000 Å. and, for the rare earth metal ions that have such bands and in regions that are not masked by the quinolinol, much weaker but sharply defined 4f transition absorption bands (257, 370). The formation of these compounds occurs in steps in dioxane solution (158). The cerium(III) derivative of 8-quinolinol is readily oxidized to the cerium(IV) compound by atmospheric oxygen (292). A report of the stabilization of neodymium(IV) by 8-quinolinol derivatives (387) is apparently in error (463).

Water-insoluble compounds with the same colors as the hydrated rare earth metal cations are precipitated from buffered solutions containing 1,3-diketones (451, 460, 474, 581). Although compounds of the apparent composition $\text{Ln}(\text{diket})_3$ are obtainable at controlled pH (460), basic derivatives are also obtained (61). When prepared in this way, these chelates are invariably hydrates, most commonly 1- or 3-hydrates (451, 474), and complete removal of water causes decomposition. They

TABLE I
A CLASSIFICATION OF TYPICAL COMPLEX SPECIES

Class	Oxidation state of metal	Examples ^a	Ref.	
Ion-pair association (in solution)	+2	None described		
	+3	LnX^{2+} (X = F, Cl, Br, I)	88, 306, 355, 407, 417, 427, 491	
		LnCl_2^+ , LnBr_2^+	88	
		LnClO_4^{2+}	212	
		LnSO_3^+	354	
		LnSO_4^+	50, 94, 526	
		LnNO_3^{2+}	94, 153, 407, 427	
		LnPO_4	354	
		$\text{Ln}(\text{C}_2\text{H}_3\text{O}_2)_n^{(3-n)+}$ (n = 1-3)	167, 286, 518	
		LnC_2O_4^+	21, 98, 99, 172	
		CeOH^{3+}	204	
		$\text{Ce}(\text{SO}_4)_n^{(4-2n)+}$	205, 379	
	Isolable adducts	+3	$\text{LnCl}_3 \cdot x\text{NH}_3$ (x = 1-8)	135
		$\text{LnCl}_3 \cdot x\text{CH}_3\text{NH}_2$ (x = 1-5)	453, 612	
		$\text{Ln}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \text{tu} \cdot 2\text{H}_2\text{O}$	477	
		$\text{Ln}(\text{SCN})_3 \cdot 6\text{ur} \cdot 8\text{H}_2\text{O}$	117	
		$\text{Ln}_2(\text{S}_4\text{O}_6)_3 \cdot 4\text{ur}$	115	
		$\text{LnX}_3 \cdot 6\text{ap}$ (X = SCN, I, ClO_4)	117, 262, 338, 340, 472	
		$\text{Ln}_2(\text{Z})_3 \cdot 6\text{ap}$ (Z = S_2O_6 , S_4O_6)	115, 117	
		$\text{Ln}(\text{NO}_3)_3 \cdot 3\text{pd}$	472	
		$\text{Ln}(\text{ClO}_4)_3 \cdot 4\text{diox} \cdot 9\text{H}_2\text{O}$	590	
		$\text{Ln}(\text{NO}_3)_3 \cdot 3\text{TBP}$	496	
		$\text{Ln}[\text{Cr}(\text{NCS})_6] \cdot 6\text{py}$	494	
		$\text{Ln}[\text{Cr}(\text{NCS})_6] \cdot 6\text{quin}$	494	
Chelates, in solution or isolable		+2	$\text{Eu}(\text{EDTA})^{2-}$	403
			$\text{Eu}(\text{DCTA})^{2-}$	230, 242
			$\text{Eu}[\text{H}(\text{ClMP})_2][\text{HClMP}]_2$	423
		+3	$\text{Ln}(\text{on})_3$	40, 257
			$\text{Ln}(\text{diket})_3 \cdot x\text{H}_2\text{O}$ (x = 1-3)	257, 451, 460, 474, 581
		$(\text{pipH})[\text{Ln}(\text{diket})_4]$	620a	
		$\text{Ln}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_4 \cdot 2\text{HC}_2\text{H}_3\text{O}_2$	490	
		$\text{Ln}(\text{RCHOHCO}_2)_n^{(3-n)+}$ (n = 1-4)	85, 235a, 454, 521	
		$\text{Ln}(\text{mal})^+$	104	
		$\text{Ln}(\text{cit})_n^{(3-3n)+}$ (n = 1-3)	24, 51, 314, 471, 492	
		$\text{Ln}(\text{gluc})^{2+}$	295, 296	
		$\text{Ln}(\text{naphth})^{2+}$	374	
		$\text{Ln}(\text{aliz})^{2+}$	493	
		$\text{Ln}(\text{alizR})_2^+$	271	
		$\text{Ln}(\text{cup})^{2+}$	452	
		$\text{Ln}(\text{C}_2\text{O}_4)_3^{3-}$	98, 99, 409	
		$\text{Ln}(\text{EDTA})^-$	67, 287, 328, 363, 372	
		$\text{Ln}(\text{DCTA})^-$	368, 369	
		$\text{Ln}(\text{HEDTA})$	364, 368, 455	
		$\text{Ln}(\text{NTA})_n^{(3-3n)+}$ (n = 1, 2)	8, 365	
		$\text{Ln}(\text{DTPA})^{2-}$	203, 375	
		$\text{Ln}(\text{IMDA})^+$	567	
		$\text{Ln}(\text{HEDTA})(\text{IMDA})^{2-}$	569	
	$\text{Ln}(\text{HEDTA})(\text{OH})^-$	198, 570		
	$\text{Ln}(\text{P}_3\text{O}_{10})^{3-}$	175, 176, 468		
	$\text{Ln}(\text{P}_2\text{O}_7)_n^{(3-4n)+}$ (n = 1, 2)	132, 176, 177		
	$\text{Ln}(\text{S}_2\text{O}_3)_3^{3-}$	116		
+4	$\text{Ce}(\text{on})_4$	257, 292, 441		
	$\text{Ce}(\text{diket})_4$	185, 474, 627		
	$\text{Ce}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$	414		
	$\text{Ce}_2(\text{gluc})_3(\text{OH})_6^{4-}$	481		
	$\text{Ce}(\text{cup})_4$	19		
Miscellaneous (largely halo)	+3	M^1LnF_4 , M^1_3LnF_6	105, 320	
	+4	M^1_2CeF_6 , M^1_3CeF_7	241	
		M^1PrF_5 , M^1_2PrF_6 , M^1_3PrF_7	15, 238, 239	
		Cs_3NdF_7	13	
		Cs_3TbF_7	240	

TABLE I (Continued)

Class	Oxidation state of metal	Examples ^a	Ref.
Miscellaneous (largely halo)	+4	Cs ₃ DyF ₇	13
		H ₂ CeCl ₆ ·4diox	381
		(pipH) ₂ CeCl ₆	380
		[(CH ₃) ₄ N] ₂ CeCl ₆	97
		[(CH ₃) ₂ NH ₂] ₈ [CeMo ₁₂ O ₄₂]·20H ₂ O	22

^a Abbreviations: Ln, yttrium or any rare earth element; tu, thiourea; ur, urotropine; ap, antipyrine; pd, pyramidone; diox, dioxane; TBP, tri-*n*-butyl phosphate; py, pyridine; quin, quinoline; EDTA, ethylenediamine-*N,N,N',N'*-tetraacetate; DCTA, 1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate; HCIMP, *n*-octyl hydrogen chloromethylphosphonate; on, 8-quinolinolate; diket, 1,3-diketone; pip, piperidine; mal, malate; cit, citrate; gluc, gluconate; naphth, naphthazarinate; aliz, alizarinate; alizR, alizarinate R; cup, cupferrate; HEDTA, *N'*-(2-hydroxyethyl)ethylenediamine-*N,N,N'*-triacetate; NTA, nitrilotriacetate; DTPA, diethylenetriamine-*N,N,N',N',N''*-pentaacetate; IMDA, imidodiacetate.

dissolve in benzene, chloroform, and other nonpolar solvents to give monomeric solutions (581), the absorption spectra of which resemble those of the hydrated ions but differ markedly in band intensity and fine structure (377). By adsorption on *D*-lactose and selective elution with benzene-petroleum ether, both yttrium and gadolinium acetylacetonates have been partially resolved into enantiomers (367). The cerium(IV) compounds are anhydrous (185, 474, 627).

Typical of the chelated species that are ions are the hydroxycarboxylates, the aminopolycarboxylates, and the polyphosphates. Many of these anions have been used in the ion-exchange separations of yttrium and the rare earth metal ions, where differences in stability of a given type of chelate with respect to the uncomplexed cations are important (section V). Although complexes derived from α -hydroxycarboxylic acids and from polyhydroxypolycarboxylic acids are common in solution (24, 51, 85, 104, 295, 296, 314, 454, 471, 492, 521), only a few solid salts, among them Na[La(cit)(OH)]·2H₂O (471), have been described. There are no data on the structures of these compounds.

The simple α -aminocarboxylic acids give derivatives that are more salt-like than complex in character (591). The aminopolycarboxylate (*e.g.*, IMDA, NTA) and polyaminepolycarboxylate (*e.g.*, EDTA, DCTA, DTPA) complexes are of particular importance in ion-exchange separations (section V) as a consequence of the rather sizable differences in formation constants between derivatives of adjacent cations in the rare earth metal series (Table II). The best-characterized solid compounds have the compositions HLn(EDTA)·*n*-H₂O (67, 221, 287, 346, 363, 372, 385), M^ILn(EDTA)·*m*H₂O (67, 346, 363, 372, 591), Ln(HEDTA)·*x*H₂O (368), Na₃Ln(NTA)₂ (32), and Ba[Ln(DCTA)]₂·*y*H₂O (368). In aqueous solution, these complex species are quite generally resistant to destruction by alkalis and other reagents, although there is evidence for the addition of hydroxide ion to at least EDTA (385, 403) and HEDTA (198, 570) complexes. Attempts to resolve the potentially asymmetric Ln(EDTA)(H₂O)₂⁻ species through crystallization of alkaloid salts have been unsuccessful (346, 372). The absorption spectra of these

anions in aqueous solution are comparable with those reported for nonaqueous solutions of the 1,3-diketone chelates (363, 368, 372, 385).

The polyphosphate species (132, 175-177, 468) are known in solution but only as a limited number of solid substances such as M^ICe(P₂O₇) (132, 175, 177), M^I₆Ce₂(P₂O₇)₃ (132), and Ce₅(P₃O₁₀)₃ (175). The crystal structures of these compounds have not been determined.

4. Miscellaneous Species

The compounds listed in Table I are known in the solid state, but their existence in solution is doubtful in all but the last case (22). The tripositive ions have little tendency to form halo complexes. Compositions deduced from the thermal analysis of MF-LnF₃ systems have no existence as such in solution. Even in crystals, species such as LnF₄⁻ are probably not distinguishable. The fluorocerate(IV) species are obtained in the solid state by fluorination of alkali metal halide-cerium(IV) oxide mixtures (241). Crystals of the composition H₂CeCl₆·4diox, obtained by the reaction of cerium(IV) oxide with dry hydrogen chloride in dioxane (381), are converted in methanol to various amine salts (380, 381). The fluoro salts containing tetrapositive praseodymium, neodymium, terbium, and dysprosium (14, 15, 238-240) are of particular importance in exemplifying stabilization of this oxidation state. The existence of a 12-molybdocerate(IV) anion (22) suggests that other heteropoly species may be formed also.

5. π -Complex Species

The absorption spectra of solutions of certain rare earth metal laurates in mesitylene have been interpreted as indicating some association of the cations with the hydrocarbon through π -electrons supplied by the latter (268). There is no confirmatory evidence. The cyclopentadienides, Ln(cp)₃ and Ln(cp)₂Cl, are salts (47, 331).

B. COORDINATION NUMBER

Many, but not all, of the compositions recorded in Table I are consistent with assignment of coordination number six to yttrium and the rare earth metal ions.

TABLE II (Continued)
 $C_4H_6O_6$, $HO_2CCH(OH)CH_2CO_2H$, Malic Acid: H_2L

Metal	Method	I	T, °C.	pK of		Log K_1	Log K_2	Log β_2	Log K_3	Log β_3	Ref.
				H ₁ L	HL ⁻						
La ³⁺	gl	0.12 M KCl	21-22	3.34	4.81	4.38	104
La ³⁺	gl	0.1 M KCl	30	3.22	4.78	4.73	3.22	7.95	2.68	10.63	79, 574
Ce ³⁺	gl	0.1 M KCl	30	3.22	4.78	5.00	3.78	8.28	2.75	11.03	79, 574
Pr ³⁺	gl	0.1 M KCl	30	3.22	4.78	5.04	3.40	8.44	2.80	11.24	79, 574
Nd ³⁺	gl	0.1 M KCl	30	3.22	4.78	5.12	3.64	8.76	2.92	11.68	79, 574
Yb ³⁺	gl	0.12 M KCl	21-22	3.34	4.81	4.92	104

 $C_4H_6O_6$, $[CH(OH)CO_2H]_2$, Tartaric Acid: H_2L

Metal	Method	I	T, °C.	pK of		Log K_1	Log K_2	Log β_2	Log K_{MHL}	Ref.
				H ₁ L	HL ⁻					
La ³⁺	...	0.2	25	2.951	3.975	3.06	1.19	635
Eu ³⁺	dist	→0	20	...	4.366	4.98	3.13	8.11	...	333

 $C_4H_8O_5$, $CH_3CH_2CH(OH)CO_2H$, α -Hydroxybutyric Acid: HL

Metal	Method	I	T, °C.	pK or HL	Log K_1	Log K_2	Log β_2	Log K_3	Log β_3	Ref.
Y ³⁺	i. ex	0.2 M NaClO ₄	3.11	2.49	5.60	1.70	7.30	533

 $C_4H_8O_5$, $CH_3C(CH_3)(OH)CO_2H$, α -Hydroxyisobutyric Acid: HL

Metal	Method	I	T, °C.	pK of HL	Log K_1	Log K_2	Log β_2	Log K_3	Log β_3	Ref.
Ce ³⁺	gl	0.1 M NaClO ₄	20	3.79	2.80	1.94	4.74	1.20	5.94	285
Ce ³⁺	qh	2(NaClO ₄)	25	...	2.43	1.89	4.32	1.00	5.32	85, 89
Ce ³⁺	dist	0% dioxane	2.43	602
Ce ³⁺	dist	60% dioxane	3.63	602
Pr ³⁺	gl	0.1 M NaClO ₄	20	3.79	2.84	2.06	4.90	1.30	6.20	285
Nd ³⁺	gl	0.1 M NaClO ₄	20	3.79	2.88	2.15	5.03	1.28	6.31	285
Nd ³⁺	qh	2(NaClO ₄)	25	...	2.62	2.05	4.67	1.40	6.07	85, 89
Sm ³⁺	gl	0.1 M NaClO ₄	20	3.79	2.99	2.39	5.38	1.38	6.76	286
Sm ³⁺	qh	2(NaClO ₄)	25	...	2.75	2.15	4.90	1.58	6.48	85, 89
Eu ³⁺	gl	0.1 M NaClO ₄	20	3.79	3.09	2.45	5.54	1.78	7.32	285
Eu ³⁺	qh	2(NaClO ₄)	25	...	2.70	2.24	4.94	1.58	6.52	85, 89
Gd ³⁺	gl	0.1 M NaClO ₄	20	3.79	3.08	2.44	5.52	1.67	7.19	285
Gd ³⁺	qh	2(NaClO ₄)	25	...	2.82	2.33	5.15	1.62	6.77	85, 89
Tb ³⁺	gl	0.1 M NaClO ₄	20	3.79	3.11	2.52	5.63	1.80	7.43	285
Tb ³⁺	qh	2(NaClO ₄)	25	...	2.83	2.42	5.25	1.78	7.03	85, 89
Dy ³⁺	gl	0.1 M NaClO ₄	20	3.79	3.27	2.62	5.89	1.97	7.86	285
Ho ³⁺	gl	0.1 M NaClO ₄	20	3.79	3.31	2.67	5.98	1.98	7.96	285
Ho ³⁺	qh	2(NaClO ₄)	25	...	3.05	2.59	5.64	2.03	7.67	85, 89
Er ³⁺	gl	0.1 M NaClO ₄	20	3.79	3.35	2.69	6.04	2.09	8.13	285
Er ³⁺	qh	2(NaClO ₄)	25	...	3.07	2.66	5.73	2.07	7.80	85, 89
Tm ³⁺	gl	0.1 M NaClO ₄	20	3.79	3.51	2.70	6.21	2.17	8.38	285
Yb ³⁺	gl	0.1 M NaClO ₄	20	3.79	3.64	2.78	6.42	2.27	8.69	285
Yb ³⁺	qh	2(NaClO ₄)	25	...	3.15	2.85	6.00	2.12	8.12	85, 89
Lu ³⁺	gl	0.1 M NaClO ₄	20	3.79	3.66	2.80	6.46	2.35	8.81	285
Y ³⁺	gl	0.1 M NaClO ₄	20	3.79	3.20	2.59	5.79	1.72	7.51	285
Y ³⁺	qh	2(NaClO ₄)	25	...	2.86	2.58	5.44	1.86	7.30	85, 89
Y ³⁺	dist	0% dioxane	3.15	602
Y ³⁺	dist	40% dioxane	4.34	602

 $C_4H_6O_4S$, $HO_2CCH_2CH(SH)CO_2H$, Thiomalic Acid: H_2L

Metal	Method	I	T, °C.	pK of		Log K_1	Log K_2	Log β_2	Log K_3	Log β_3	Ref.
				H ₁ L	HL ⁻						
La ³⁺	gl	0.1 M KCl	30	3.15	4.68	3.01	2.57	5.58	2.27	7.85	79, 574
Ce ³⁺	gl	0.1 M KCl	30	3.15	4.68	3.22	2.88	6.10	2.53	8.63	79, 574
Pr ³⁺	gl	0.1 M HCl	30	3.15	4.68	3.31	2.86	6.17	2.59	8.76	79, 574
Nd ³⁺	gl	0.1 M KCl	30	3.15	4.68	3.38	2.99	6.37	2.57	8.94	79, 574

 $C_4H_7O_4N$, $HN(CH_2CO_2H)_2$, Iminodiacetic Acid: H_2L

Metal	Method	I	T, °C.	pK of		Log K_1	Log K_2	Log β_2	Ref.
				H ₂ L	HL ⁻				
La ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	5.88	4.09	9.97	154
La ³⁺	gl	0.1 M KCl	25	5.90	54
Ce ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	6.18	4.53	10.71	154
Pr ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	6.44	4.78	11.22	567
Pr ³⁺	gl	0.1 M KCl	25	6.87	203
Nd ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	6.50	4.89	11.39	567
Nd ³⁺	gl	0.1 M KCl	25	6.94	203
Sm ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	6.64	5.24	11.88	567
Sm ³⁺	gl	0.1 M KCl	25	7.10	203
Eu ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	6.73	5.38	12.11	567
Eu ³⁺	gl	0.1 M KCl	25	7.26	203
Gd ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	6.68	5.39	12.07	567
Gd ³⁺	gl	0.1 M KCl	25	7.02	203
Tb ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	6.78	5.46	12.24	567

TABLE II (Continued)

Metal	Method	I	T, °C.	pK of		Log K ₁	Log K ₂	Log β ₁	Ref.
				H ₂ L	HL ⁻				
Tb ³⁺	gl	0.1 M KCl	25	7.20	203
Dy ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	6.88	5.43	12.31	567
Dy ³⁺	gl	0.1 M KCl	25	7.32	203
Ho ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	6.97	5.50	12.47	567
Er ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	7.09	5.59	12.68	567
Er ³⁺	gl	0.1 M KCl	25	7.40	203
Tm ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	7.22	5.68	12.90	567
Tm ³⁺	gl	0.1 M KCl	25	7.50	203
Yb ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	7.42	5.85	13.27	567
Yb ³⁺	gl	0.1 M KCl	25	7.73	203
Lu ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	7.61	6.12	13.73	567
Y ³⁺	gl	0.1 M KNO ₃	25	2.58	9.33	6.78	5.25	12.03	567
Y ³⁺	gl	0.1 M KCl	25	7.11	203

Metal	Method	I	T, °C.	pK of		Log K ₁	Log K ₂	Log β	Log K ₃	Log β ₃	Ref.
				H ₂ L	HL ⁻						
La ³⁺	gl	0.1 M KCl	25	3.87	9.87	5.0	4.2	27
La ³⁺	gl	0.1 M KCl	30	3.79	9.63	4.84	3.42	8.26	79, 574
Ce ³⁺	gl	0.1 M KCl	25	3.87	9.87	5.2-5.3	4.6	27
Ce ³⁺	gl	0.1 M KCl	30	3.79	9.63	5.13	3.65	8.78	2.75	11.53	79, 574
Pr ³⁺	gl	0.1 M KCl	25	3.87	9.87	5.4-5.5	4.8	27
Pr ³⁺	gl	0.1 M KCl	30	3.79	9.63	5.23	3.84	9.07	2.72	11.79	79, 574
Nd ³⁺	gl	0.1 M KCl	25	3.87	9.87	5.5-5.6	4.9	27
Nd ³⁺	gl	0.1 M KCl	30	3.79	9.63	5.40	4.08	9.48	3.06	12.54	79, 574

Metal	Method	I	T, °C.	pK of HL		log K ₁	Log K ₂	Log β ₁	Log K ₃	Log β ₃	Ref.
				H ₂ L	HL ⁻						
La ³⁺	gl	75% acetone	..	9.80	6.15	4.67	10.82	3.68	14.50	111	
La ³⁺	gl	0.1 M NaClO ₄	30	8.88	4.96	3.45	8.41	2.5	10.91	191	
Ce ³⁺	gl	0.1 M NaClO ₄	30	8.88	5.09	3.3	8.39	2.9	11.29	191	
Pr ³⁺	gl	75% acetone	..	9.80	6.91	5.63	12.54	4.51	17.05	112	
Pr ³⁺	gl	0.1 M NaClO ₄	30	8.88	5.27	3.93	9.20	3.2	12.40	191	
Nd ³⁺	gl	75% acetone	..	9.80	6.91	5.65	12.56	4.54	17.10	112	
Nd ³⁺	gl	0.1 M NaClO ₄	30	8.88	5.30	4.10	9.40	3.20	12.60	191	
Sm ³⁺	gl	0.1 M NaClO ₄	30	8.88	5.59	4.46	10.05	2.90	12.95	191	
Eu ³⁺	gl	0.1 M NaClO ₄	30	8.88	5.87	4.48	10.35	3.29	13.64	191	
Gd ³⁺	gl	0.1 M NaClO ₄	30	8.88	5.90	4.48	10.38	3.41	13.79	191	
Tb ³⁺	gl	0.1 M NaClO ₄	30	8.88	6.02	4.61	10.63	3.41	14.04	191	
Dy ³⁺	gl	0.1 M NaClO ₄	30	8.88	6.03	4.67	10.70	3.34	14.04	191	
Ho ³⁺	gl	0.1 M NaClO ₄	30	8.88	6.05	4.68	10.73	3.40	14.13	191	
Er ³⁺	gl	0.1 M NaClO ₄	30	8.88	5.99	4.68	10.67	3.38	14.05	191	
Tm ³⁺	gl	0.1 M NaClO ₄	30	8.88	6.09	4.76	10.85	3.48	14.33	191	
Yb ³⁺	gl	0.1 M NaClO ₄	30	8.88	6.18	4.86	11.04	3.60	14.64	191	
Lu ³⁺	gl	0.1 M NaClO ₄	30	8.88	6.23	4.77	11.00	3.63	14.63	191	
Y ³⁺	gl	75% acetone	..	9.80	7.73	6.00	13.73	4.77	18.50	111	
Y ³⁺	gl	0.1 M NaClO ₄	30	8.88	5.87	4.98	10.85	3.25	14.10	191	

Metal	Method	I	T, °C.	pK of		Log K ₁	Log K ₂	Log β ₂	Log K ₃	Log β ₃	Ref.
				H ₂ L	HL ⁻						
Ce ³⁺	gl	...	20	4.0	103	
Nd ³⁺	gl	...	20	4.0	103	
Sm ³⁺	gl	...	20	4.0	103	

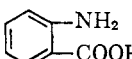
Metal	Method	I	T, °C.	pK of HL	Log K ₁	Log K ₂	Log β ₂	Log K ₃	Log β ₃	Ref.
Y ³⁺	i. ex	0.2 M NaClO ₄	2.60	2.35	4.95	533

Metal	Method	I	T, °C.	pK of		Log β ₂	Log K ^H _{MH₂L₂}	Log K ^H _{MHL₂}	Log K ^H _{MHL₂}	Ref.
				H ₂ L	HL ⁻					
La ³⁺	em ^d	→0	20	9.45	6.97	4.20	4.32	539
Ce ³⁺	em ^d	→0	20	9.65	6.18	4.18	4.20	539
Ce ³⁺	i. ex	...	25	7.72	314
Nd ³⁺	em ^d	→0	20	9.70	6.32	4.18	4.20	539
Pm ³⁺	em ^d	→0	20	9.75	6.36	4.18	4.20	539
Eu ³⁺	em ^d	→0	20	9.80	6.46	4.18	4.15	539
Yb ³⁺	gl	8.00	492

Metal	Method	I	T, °C.	pK of HL		Log K ₁	Log K ₂	Log β ₂	Log K ₃	Log β ₃	Ref.
				H ₂ L	HL ⁻						
La ³⁺	gl	75% acetone	...	9.74	6.22	4.87	11.09	4.16	15.25	114	
Pr ³⁺	gl	75% acetone	...	9.74	6.72	5.84	12.56	5.38	17.94	114	
Nd ³⁺	gl	75% acetone	...	9.74	6.94	6.24	13.18	5.01	18.19	114	
Y ³⁺	gl	75% acetone	...	9.74	7.19	6.04	13.23	5.32	18.55	114	

TABLE II (Continued)
 $C_6H_{11}O_7$. $HO_2C[CH(OH)]_4CH_2OH$. Gluconic Acid: HL

Metal	Method	I	T, °C.	pK of HL	Log K ₁	Log K ₂	Log β ₁	Log K ₃	Log β ₂	Log K ^{H_ML}	Log K ^{H_MLOH}	Ref.
La ³⁺	gl	2.60	4.04	11.30	296
La ³⁺	i. ex	0.23 M NH ₄ Cl	...	3.56	2.38	1.90	4.28	1.42	5.70	297
Ce ³⁺	gl	2.62	296
Nd ³⁺	gl	2.72	3.73	9.96	296
Nd ³⁺	i. ex	0.23 M NH ₄ Cl	...	3.56	2.7	2.36	5.06	1.94	7.00	298
Sm ³⁺	gl	2.82	3.48	9.66	296
Gd ³⁺	gl	2.77	3.63	9.36	296
Yb ³⁺	gl	2.58	8.05	296
Yb ³⁺	i. ex	0.23 M NH ₄ Cl	...	3.56	3.3	3.22	6.52	2.10	8.62	298
Y ³⁺	gl	2.60	4.30	9.17	296

 $C_7H_7O_2N$.  Anthranilic Acid: HL

Metal	Method	I	T, °C.	pK of HL	Log K ₁	Log K ₂	Log β ₁	Ref.
La ³⁺	gl	0.1 M KCl	30	4.86	3.14	79, 574
Ce ³⁺	gl	0.1 M KCl	30	4.86	3.18	79, 574
Pr ³⁺	gl	0.1 M KCl	30	4.86	3.22	79, 574
Nd ³⁺	gl	0.1 M KCl	30	4.86	3.23	79, 574

 $C_5H_9O_4N$. $N(CH_2CO_2H)_3$. Nitritotriacetic Acid: H₃L

Metal	Method	I	T, °C.	pK of			Log K ₁	Log K ₂	Log β ₁	Ref.
				H ₃ L	HL ²⁻	HL ⁻				
La ³⁺	gl	0.1 M KCl	20	1.89	2.49	9.73	...	7.37	...	8
La ³⁺	pol	0.1 M KNO ₃	20	9.73	9.87	7.39	17.26	319
La ³⁺	gl	0.1 M KNO ₃	25	9.75	10.36	7.24	17.60	365
Ce ³⁺	gl	0.1 M KCl	20	1.89	2.49	9.73	...	7.98	...	8
Ce ³⁺	pol	0.1 M KNO ₃	20	9.73	10.43	7.75	18.18	319
Ce ³⁺	gl	0.1 M KNO ₃	25	9.75	10.83	7.84	18.67	365
Pr ³⁺	sp	~0.02	18-20	10.30	8.95	19.25	17
Pr ³⁺	gl	0.1 M KCl	20	1.89	2.49	9.73	...	8.18	...	8
Pr ³⁺	pol	0.1 M KNO ₃	20	9.73	10.93	8.31	19.24	319
Pr ³⁺	gl	0.1 M KNO ₃	25	9.75	11.07	8.18	19.25	365
Nd ³⁺	sp	~0.02	18-20	10.49	8.98	19.47	17
Nd ³⁺	gl	0.1 M KCl	20	1.89	2.49	9.73	...	8.44	...	8
Nd ³⁺	pol	0.1 M KNO ₃	20	9.73	11.13	8.52	19.65	319
Nd ³⁺	gl	0.1 M KNO ₃	25	9.75	11.26	8.47	19.73	365
Sm ³⁺	sp	~0.02	18-20	10.79	9.78	20.57	17
Sm ³⁺	gl	0.1 M KCl	20	1.89	2.49	9.73	...	9.15	...	8
Sm ³⁺	pol	0.1 M KNO ₃	20	9.73	11.38	8.96	20.34	319
Sm ³⁺	gl	0.1 M KNO ₃	25	9.75	11.53	9.00	20.53	365
Eu ³⁺	pol	0.1 M KNO ₃	20	9.73	11.35	9.17	20.52	319
Eu ³⁺	gl	0.1 M KNO ₃	25	9.75	11.52	9.18	20.70	365
Gd ³⁺	gl	0.1 M KCl	20	1.89	2.49	9.73	...	9.36	...	8
Gd ³⁺	pol	0.1 M KNO ₃	20	9.73	11.17	9.21	20.38	319
Gd ³⁺	gl	0.1 M KNO ₃	25	9.75	11.54	9.26	20.80	365
Tb ³⁺	pol	0.1 M KNO ₃	20	9.73	11.31	9.34	20.65	319
Tb ³⁺	gl	0.1 M KNO ₃	25	9.75	11.59	9.38	20.97	365
Dy ³⁺	gl	0.1 M KCl	20	1.89	2.49	9.73	...	9.40	...	8
Dy ³⁺	pol	0.1 M KNO ₃	20	9.73	11.38	9.27	20.65	319
Dy ³⁺	gl	0.1 M KNO ₃	25	9.75	11.74	9.41	21.15	365
Ho ³⁺	pol	0.1 M KNO ₃	20	9.73	11.53	9.23	20.76	319
Ho ³⁺	gl	0.1 M KNO ₃	25	9.75	11.90	9.35	21.25	365
Er ³⁺	pol	0.1 M KNO ₃	20	9.73	11.66	9.11	20.77	319
Er ³⁺	gl	0.1 M KNO ₃	25	9.75	12.03	9.26	21.29	365
Tm ³⁺	pol	0.1 M KNO ₃	20	9.73	11.79	9.05	20.84	319
Tm ³⁺	gl	0.1 M KNO ₃	25	9.75	12.22	9.23	21.45	365
Yb ³⁺	gl	0.1 M KCl	20	1.89	2.49	9.73	...	9.22	...	8
Yb ³⁺	pol	0.1 M KNO ₃	20	9.73	11.98	9.07	21.05	319
Yb ³⁺	gl	0.1 M KNO ₃	25	9.75	12.40	9.29	21.69	365
Lu ³⁺	pol	0.1 M KNO ₃	20	9.73	12.10	9.16	21.26	319
Lu ³⁺	gl	0.1 M KNO ₃	25	9.75	12.49	9.42	21.91	365
Y ³⁺	gl	0.1 M KCl	20	1.89	2.49	9.73	...	9.02	...	8
Y ³⁺	pol	0.1 M KNO ₃	20	9.73	11.23	8.99	20.22	319
Y ³⁺	gl	0.1 M KNO ₃	25	9.75	11.48	8.95	20.43	365

 $C_6H_{11}O_6N$. $HOCH_2CH_2N(CH_2CO_2H)_2$. N-2-Hydroxyethyliminodiacetic Acid: H₂L

Metal	Method	I	T, °C.	pK of		Log K ₁	Log K ^{H_ML}	Ref.
				H ₂ L	HL ⁻			
La ³⁺	gl	0.1	25	8.5	96

 $C_6H_{12}O_4N_2$. $HO_2CCH_2NH[CH_2]_2NHCH_2CO_2H$. Ethylenediamine-N,N'-diacetic Acid: H₂L

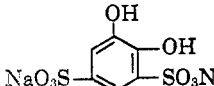
Metal	Method	I	T, °C.	pK of		Log K ₁	Log K ₂	Log β ₁	Ref.
				H ₂ L	HL ⁻				
La ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	7.04	4.73	11.77	568
Ce ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	7.48	4.92	12.35	568
Pr ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	7.84	5.23	13.07	568
Nd ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	8.06	5.63	13.69	568
Sm ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	8.28	6.07	14.35	568
Eu ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	8.38	6.35	14.73	568

TABLE II (Continued)

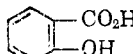
Metal	Method	I	T, °C.	pK of		Log K ₁	Log K ₂	Log β ₂	Ref.
				H ₂ L	HL ⁻				
Gd ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	8.13	6.08	14.21	568
Tb ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	8.18	6.52	14.70	568
Dy ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	8.31	6.78	15.09	568
Ho ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	8.42	7.00	15.42	568
Er ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	8.59	7.45	15.78	568
Tm ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	8.75	7.64	16.39	568
Yb ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	8.93	7.92	16.85	568
Lu ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	9.09	8.48	17.57	568
Y ³⁺	gl	0.1 M KNO ₃	25	6.48	9.57	7.78	6.34	14.12	568

C₆H₁₃O₄N. HO₂CCH₂N(CH₂CH₂OH)₂. Di(2-hydroxyethyl)aminoacetic Acid: HL

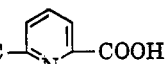
Metal	Method	I	T, °C.	pK of HL		Log K ₁	Log K ₂	Log β ₂	Ref.
				H ₂ L ²⁻	HL ⁻				
La ³⁺	gl	0.1	25	8	5.0	96
Pr ³⁺	gl	0.1 M KCl	30	8.07	5.35	3.86	9.21	634	634
Nd ³⁺	gl	0.1 M KCl	30	8.07	5.48	4.04	9.52	634	634

C₆H₄O₃S₂Na₂.  Pyrocatechol 3,5-Disodium Sulfonate: H₂L²⁻

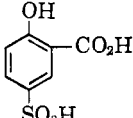
Metal	Method	I	T, °C.	pK of		Log K ₁	Log K ^H _{ML}	Ref.
				H ₂ L ²⁻	HL ⁻			
La ³⁺	gl	0.1	25	12.9	8.3	96

C₇H₅O₃.  Salicylic Acid: HL

Metal	Method	I	T, °C.	pK of HL	Log K ₁	Log	Log	Ref.
						K ^H _{ML}	K ^H _{ML(OH)}	
La ³⁺	gl	...	20-22	7.52	10.0	144 ^a
La ³⁺	gl	0.1 M KCl	30	2.88	2.64	79, 574
Ce ³⁺	gl	0.1 M KCl	30	2.88	2.66	79, 574
Pr ³⁺	gl	0.1 M KCl	30	2.88	2.68	79, 574
Nd ³⁺	gl	0.1 M KCl	30	2.88	2.70	79, 574

C₇H₅O₄N.  2,6-Pyridinedicarboxylic Acid (Dipicolinic Acid): H₂L

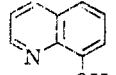
Metal	Method	I	T, °C.	pK of		Log K ₁	Log K ₂	Log β ₂	Log K ₁	Log β ₁	Ref.
				H ₂ L	HL ⁻						
La ³⁺	Cu-Hg	0.5 M NaClO ₄	20	7.98	5.81	13.79	4.27	18.06	187
Ce ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.34	6.08	14.42	4.38	18.80	187
Pr ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.63	6.47	15.10	4.84	19.94	187
Nd ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.78	6.72	15.50	5.06	20.56	187
Sm ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.86	7.02	15.88	5.35	21.23	187
Eu ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.84	7.14	15.98	5.51	21.49	187
Gd ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.74	7.32	16.06	5.77	21.83	187
Tb ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.68	7.43	16.11	5.92	22.03	187
Dy ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.69	7.49	16.18	5.95	22.13	187
Ho ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.72	7.51	16.23	5.85	22.08	187
Er ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.77	7.62	16.39	5.74	22.13	187
Tm ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.83	7.71	16.54	5.50	22.04	187
Yb ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.85	7.76	16.61	5.12	21.73	187
Lu ³⁺	Cu-Hg	0.5 M NaClO ₄	20	9.03	7.77	16.80	4.68	21.48	187
Y ³⁺	Cu-Hg	0.5 M NaClO ₄	20	8.46	7.27	15.73	5.61	21.34	187

C₇H₅O₆S.  5-Sulfosalicylic Acid: H₂L

Metal	Method	I	T, °C.	pK of			Log K ₁	Ref.
				H ₂ L	H ₂ L ⁻	HL ²⁻		
La ³⁺	gl	0.1	25	9.11	96

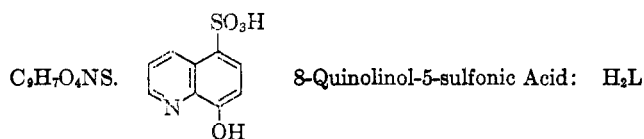
C₈H₁₆O₅P. (C₄H₉O)₂P(O)(OH). Dibutylphosphoric Acid: HL

Metal	Method	I	T, °C.	pK of HL	Log K ^b	Log K ₁	Ref.
Pr ³⁺	dist	15.4	...	497
Nd ³⁺	dist	15.0	...	497
Yb ³⁺	dist	18.6	...	497
Y ³⁺	dist	0.1 M HNO ₃	20	2.91	499

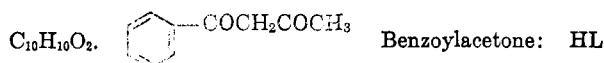
C₈H₇ON.  8-Hydroxyquinoline: HL

Metal	Method	I	T, °C.	pK of HL	Log K ₁	Log K ₂	Log β ₂	Log K ₁	Log β ₁	Ref.

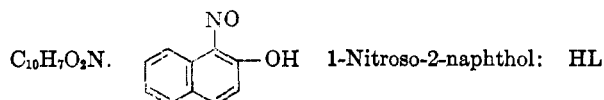
TABLE II (Continued)



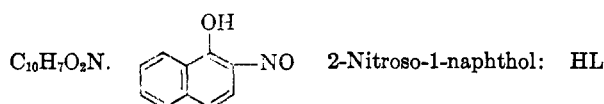
Metal	Method	<i>I</i>	<i>T</i> , °C.	pK of			Log K_1	Log K_2	Log β_1	Log K_3	Log β_3	Ref.
				H_2L	HL^-							
La ³⁺	gl	→0	25	4.01	8.53	5.63	4.5	10.13	3.7	13.83	155	
Ce ³⁺	gl	→0	25	4.01	8.53	6.05	5.0	11.05	3.9	14.95	155	
Pr ³⁺	gl	→0	25	4.01	8.53	6.17	5.20	11.37	4.3	15.67	155	
Nd ³⁺	gl	→0	25	4.01	8.53	6.3	5.3	11.6	4.4	16.00	155	
Sm ³⁺	gl	→0	25	4.01	8.53	6.58	5.70	12.28	4.76	17.04	155	
Gd ³⁺	gl	→0	25	4.01	8.53	6.64	5.73	12.37	4.9	17.27	155	
Er ³⁺	gl	→0	25	4.01	8.53	7.16	6.18	13.34	5.22	18.56	155	



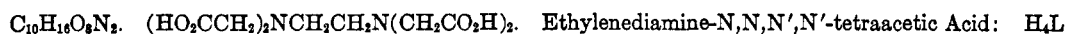
Metal	Method	<i>I</i>	<i>T</i> , °C.	pK of HL	Log K_1	Log K_2	Log β_1	Log K_3	Log β_3	Ref.
La ³⁺	gl	75% acetone	...	9.57	6.33	5.33	11.66	4.54	16.20	113
Pr ³⁺	gl	75% acetone	...	9.57	7.02	6.16	13.18	5.12	18.30	113
Y ³⁺	gl	75% acetone	...	9.57	8.24	6.74	14.98	5.59	20.57	113
Y ³⁺	dist	6.55	4.85	11.4	3.0	14.4	537



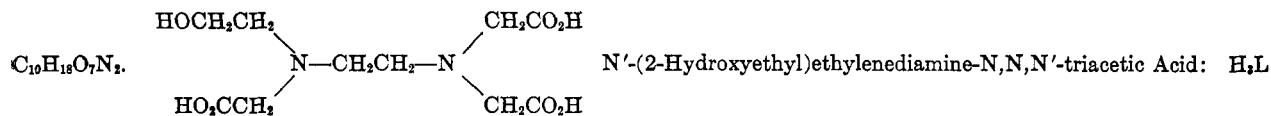
Metal	Method	<i>I</i>	<i>T</i> , °C.	pK of HL	Log K_1	Log K_2	Log β_1	Log K_3	Log β_3	Ref.
Pr ³⁺	gl	75% dioxane	30	11.62	9.04	8.02	17.60	6.79	23.85	76
Nd ³⁺	gl	75% dioxane	30	11.62	9.5	8.2	17.7	7.86	25.56	76
Y ³⁺	gl	75% dioxane	30	11.62	9.02	8.72	17.74	7.30	25.04	76



Metal	Method	<i>I</i>	<i>T</i> , °C.	pK of HL	Log K_1	Log K_2	Log β_1	Log K_3	Log β_3	Ref.
Pr ³⁺	gl	75% dioxane	30	11.14	8.48	7.3	15.78	6.36	22.14	76
Nd ³⁺	gl	75% dioxane	30	11.14	8.51	7.6	16.11	7.05	23.16	76
Y ³⁺	gl	75% dioxane	30	11.14	8.3	7.6	15.9	7.4	23.3	76



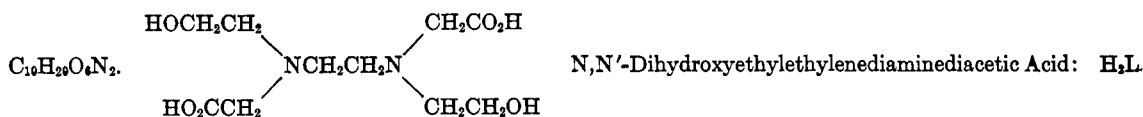
Metal	Method	<i>I</i>	<i>T</i> , °C.	pK of				Log K_1	Log $K^{H_{MHL}}$	Ref.
				H_4L	H_3L^-	H_2L^{2-}	HL^{3-}			
La ³⁺	em ^d	→0	20	2.0	2.67	6.16	10.26	16.34	...	506
Ce ³⁺	em ^d	→0	20	2.0	2.67	6.16	10.26	16.80	...	506
Ce ³⁺	sp	→0	25	2.0	2.67	6.16	10.26	16.75	...	406
Pm ³⁺	em ^d	→0	20	2.0	2.67	6.16	10.26	17.42	...	506
Pm ³⁺	i. ex	0.1 M NH ₄ Cl	25	2.0	2.67	6.16	10.26	16.18	...	73
Sm ³⁺	emf	...	25	16.43	2.12	562
Eu ³⁺	em ^d	→0	20	2.0	2.67	6.16	10.26	17.99	...	506
Y ³⁺	em ^d	→0	20	2.0	2.67	6.16	10.26	18.32	...	506



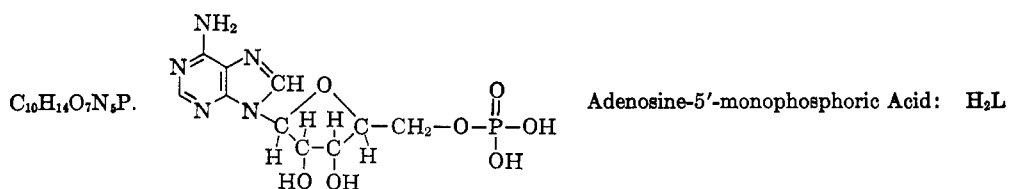
Metal	Method	<i>I</i>	<i>T</i> , °C.	pK of			Log K_1	Log $K^{H_{ML}}$	Ref.
				H_3L	H_2L^-	HL^{2-}			
La ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	13.82	...	455
La ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	13.46	...	364
La ³⁺	gl	0.1 M KNO ₃	25	10.31	198
La ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	13.22	...	532 ^d
Ce ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	14.45	...	455
Ce ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	14.11	...	364
Ce ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	14.08	...	532 ^d
Pr ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	14.96	...	455
Pr ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	14.61	...	364
Pr ³⁺	gl	0.1 M KNO ₃	25	10.08	198
Pr ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	14.39	...	532 ^d
Nd ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	15.16	...	455
Nd ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	14.86	...	364

TABLE II (Continued)

Metal	Method	I	T, °C.	pK of			Log K ₁	Log K ^H _{ML}	Ref.
				H ₂ L	H ₂ L ⁻	HL ²⁻			
Nd ³⁺	gl	0.1 M KNO ₃	25	10.18	198
Nd ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	14.71	...	532 ^o
Sm ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	15.64	...	455
Sm ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	15.28	...	364
Sm ³⁺	gl	0.1 M KNO ₃	25	10.07	198
Sm ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	15.15	...	532 ^o
Sm ³⁺	pol	0.1 M KNO ₃	25	2.91	5.41	9.90	15.3	...	532
Eu ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	15.62	...	455
Eu ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	15.35	...	364
Eu ³⁺	gl	0.1 M KNO ₃	25	9.74	198
Eu ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	15.21	...	532 ^o
Gd ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	15.44	...	455
Gd ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	15.22	...	364
Gd ³⁺	gl	0.1 M KNO ₃	25	9.79	198
Gd ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	15.10	...	532 ^o
Gd ³⁺	pol	0.1 M KNO ₃	25	2.91	5.41	9.90	15.4	...	532
Tb ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	15.55	...	455
Tb ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	15.32	...	364
Tb ³⁺	gl	0.1 M KNO ₃	25	9.25	198 ^o
Tb ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	15.10	...	532
Dy ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	15.51	...	455
Dy ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	15.30	...	364
Dy ³⁺	gl	0.1 M KNO ₃	25	8.89	198
Dy ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	15.08	...	532
Dy ³⁺	pol	0.1 M KNO ₃	25	2.91	5.41	9.90	15.3	...	532
Ho ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	15.55	...	455
Ho ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	15.32	...	364
Ho ³⁺	gl	0.1 M KNO ₃	25	8.65	198 ^o
Ho ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	15.06	...	532 ^o
Ho ³⁺	pol	0.1 M KNO ₃	25	2.91	5.41	9.90	15.4	...	532
Er ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	15.61	...	455
Er ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	15.42	...	364
Er ³⁺	gl	0.1 M KNO ₃	25	8.63	198
Er ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	15.17	...	532 ^o
Er ³⁺	pol	0.1 M KNO ₃	25	2.91	5.41	9.90	15.4	...	532
Tm ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	16.00	...	455
Tm ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	15.59	...	364
Tm ³⁺	gl	0.1 M KNO ₃	25	8.66	198
Tm ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	15.38	...	532 ^o
Tm ³⁺	pol	0.1 M KNO ₃	25	2.91	5.41	9.90	15.5	...	532
Yb ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	16.17	...	455
Yb ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	15.88	...	364
Yb ³⁺	gl	0.1 M KNO ₃	25	8.56	198
Yb ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	15.64	...	532 ^o
Yb ³⁺	pol	0.1 M KNO ₃	25	2.91	5.41	9.90	15.8	...	532
Lu ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	16.25	...	455
Lu ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	15.88	...	364
Lu ³⁺	gl	0.1 M KNO ₃	25	8.64	198
Lu ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	15.79	...	532 ^o
Lu ³⁺	pol	0.1 M KNO ₃	25	2.91	5.41	9.90	16.0	...	532
Y ³⁺	Hg	0.1 M KNO ₃	20	3.23	5.50	10.09	15.03	...	355
Y ³⁺	gl	0.1 M KNO ₃	25	2.39	5.37	9.93	14.65	...	364
Y ³⁺	gl	0.1 M KNO ₃	25	9.01	198
Y ³⁺	gl	0.1 M KCl	25	2.91	5.41	9.90	14.49	...	532 ^o
Y ³⁺	pol	0.1 M KNO ₃	25	2.91	5.41	9.90	14.8	...	532

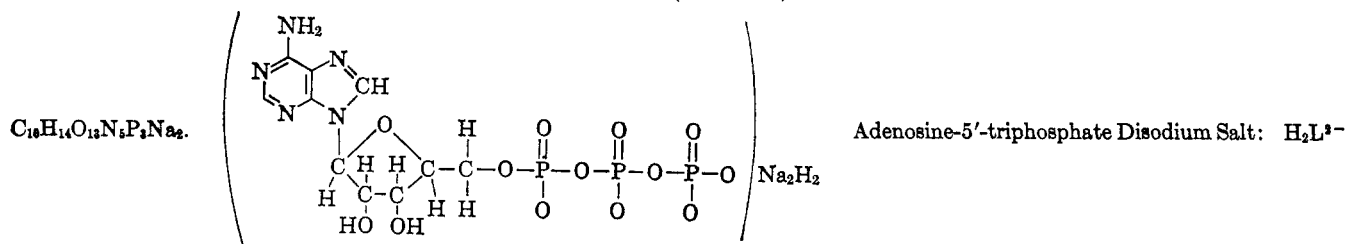


Metal	Method	I	T, °C.	pK of		Log K ₁	Log K ^H _{ML}	Ref.
				H ₂ L	HL ⁻			
La ³⁺	gl	0.1	25	9.3	8.4	96

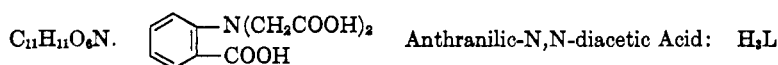


Metal	Method	I	T, °C.	pK of H ₂ L		Log β ₂	Ref.
				H ₂ L	HL ⁻		
Y ³⁺	i. ex	0.15 M NaCl	25	5.70	400

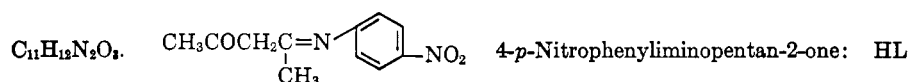
TABLE II (Continued)



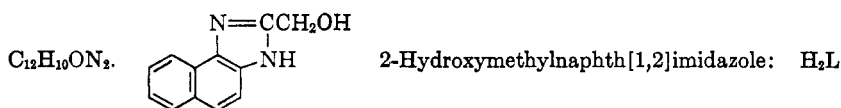
Metal	Method	<i>I</i>	<i>T</i> , °C.	p <i>K</i> of			Log β_3	Ref.
				H_2L^{2-}	HL^{1-}	L^{3-}		
Y^{3+}	i. ex	0.15 <i>M</i> NaCl	~25	11.10	400



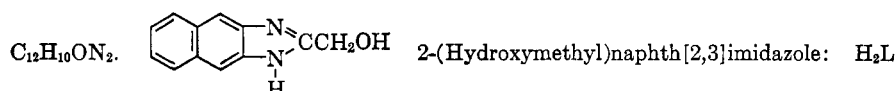
Metal	Method	<i>I</i>	<i>T</i> , °C.	p <i>K</i> of			Log K_1	Ref.
				H_2L	HL^-	L^{2-}		
La^{3+}	6.0	108



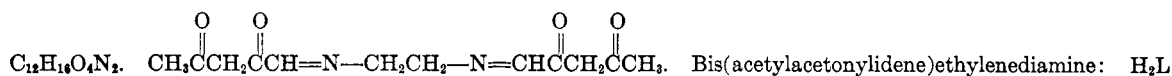
Metal	Method	<i>I</i>	<i>T</i> , °C.	p <i>K</i> of HL	Log K_1	Log K_2	Log β_2	Log K_3	Log β_3	Ref.
Sm^{3+}	gl	dioxane	30	...	10.78	9.11	19.89	8.22	27.11	465
Gd^{3+}	gl	dioxane	30	...	11.14	9.13	20.27	7.42	27.69	465
Dy^{3+}	gl	dioxane	30	...	11.12	9.10	20.22	7.38	27.60	465
Er^{3+}	gl	dioxane	30	...	11.08	9.06	20.14	7.46	27.60	465
Yb^{3+}	gl	dioxane	30	...	11.33	9.37	20.70	7.79	28.49	465



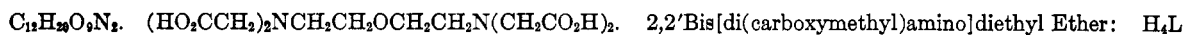
Metal	Method	<i>I</i>	<i>T</i> , °C.	p <i>K</i> of		Log K_1	Ref.
				H_2L	HL^-		
La^{3+}	gl	50% dioxane	25	4.44	12.23	7.70	312



Metal	Method	<i>I</i>	<i>T</i> , °C.	p <i>K</i> of		Log K_1	Ref.
				H_2L	HL^-		
La^{3+}	gl	50% dioxane	25	4.50	12.30	7.21	312



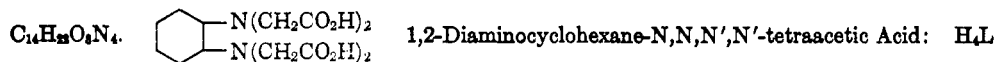
Metal	Method	<i>I</i>	<i>T</i> , °C.	p <i>K</i> of		Log K_1	Ref.
				H_2L	HL^-		
Nd^{3+}	sp	0.05	18-20	1.49	16



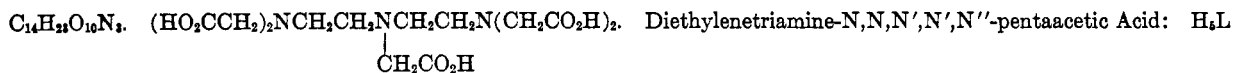
Metal	Method	<i>I</i>	<i>T</i> , °C.	p <i>K</i> of				Log K_1	Ref.
				H_4L	H_3L^-	H_2L^{2-}	HL^{3-}		
La^{3+}	Hg	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	16.00	326, 327
La^{3+}	pol	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	16.29	219, 327
Ce^{3+}	i. ex	0.5 <i>M</i> NH_4Cl	20	1.75	2.76	8.84	9.47	17.87	573
Ce^{3+}	Hg	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	16.69	326, 327
Ce^{3+}	pol	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	17.13	219, 327
Pr^{3+}	Hg	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	17.36	326, 327
Pr^{3+}	pol	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	17.61	219, 327
Nd^{3+}	Hg	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	17.67	326, 327
Nd^{3+}	pol	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	17.81	219, 327
Sm^{3+}	Hg	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	18.19	326, 327
Sm^{3+}	pol	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	18.25	219, 327
Eu^{3+}	Hg	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	18.31	326, 327
Eu^{3+}	pol	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	18.38	219, 327
Gd^{3+}	Hg	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	18.13	326, 327
Gd^{3+}	pol	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	18.21	219, 327
Tb^{3+}	Hg	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	18.31	326, 327
Tb^{3+}	pol	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	18.31	219, 327
Dy^{3+}	Hg	0.1 <i>M</i> KNO_3	20	1.75	2.76	8.84	9.47	18.21	326, 327

TABLE II (Continued)

Metal	Method	I	T, °C.	pK of				Log K ₁	Ref.
				H ₄ L	H ₃ L ⁻	H ₂ L ²⁻	HL ³⁻		
Dy ³⁺	pol	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	18.29	219, 327
Ho ³⁺	Hg	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	18.13	326, 327
Ho ³⁺	pol	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	18.17	219, 327
Er ³⁺	Hg	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	17.99	326, 327
Er ³⁺	pol	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	18.18	219, 327
Tm ³⁺	Hg	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	17.83	326, 327
Tm ³⁺	pol	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	18.01	219, 327
Yb ³⁺	Hg	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	17.85	326, 327
Yb ³⁺	pol	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	18.06	219, 327
Lu ³⁺	Hg	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	17.75	326, 327
Lu ³⁺	pol	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	17.92	219, 327
Y ³⁺	Hg	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	17.54	326, 327
Y ³⁺	pol	0.1 M KNO ₃	20	1.75	2.76	8.84	9.47	17.79	219, 327



Metal	Method	I	T, °C.	pK of				Log K ₁	Log K ^H _{MHL}	Ref.
				H ₄ L	H ₃ L ⁻	H ₂ L ²⁻	HL ³⁻			
La ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	16.18 ^b	...	269
La ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	16.35	2.24	369
Ce ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	16.96 ^b	...	269
Pr ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	17.37 ^b	...	269
Pr ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	17.23	1.35	369
Nd ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	17.66 ^b	...	269
Nd ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	17.69	2.22	369
Sm ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	18.55 ^b	...	269
Sm ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	18.63	2.18	369
Eu ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	18.99 ^b	...	269
Eu ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	18.77	2.17	369
Gd ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	19.02 ^b	...	269
Gd ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	18.80	2.23	369
Tb ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	19.58 ^b	...	269
Tb ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	19.30	2.11	369
Dy ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	20.02 ^b	...	269
Dy ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	19.69	2.16	369
Ho ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	20.27 ^b	...	269
Ho ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	19.89	2.41	369
Er ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	20.66 ^b	...	269
Er ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	20.20	2.43	369
Tm ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	20.87 ^b	...	269
Tm ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	20.46	2.20	369
Yb ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	21.33 ^b	...	269
Yb ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	20.80	2.36	369
Lu ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	21.39 ^b	...	269
Lu ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	20.91	2.31	369
Y ³⁺	pol	0.1 M KNO ₃	20	2.4	3.5	6.12	11.70	19.81 ^b	...	269
Y ³⁺	Hg	0.1 M KNO ₃	25	6.12	11.58	19.41	2.18	369



Metal	Method	I	T, °C.	pK of					Log K ₁	Log K ^H _{MHL}	Ref.
				H ₄ L	H ₄ L ⁻	H ₃ L ²⁻	H ₂ L ³⁻	HL ⁴⁻			
La ³⁺	pol	0.1 M KNO ₃	20	19.35	...	252
La ³⁺	gl	0.1 M KCl	25	1.79	2.56	4.42	8.76	10.42	19.96	2.8	203
La ³⁺	Hg	0.1 M KNO ₃	25	2.08	2.41	4.26	8.60	10.55	19.1	...	235
La ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	19.48	2.60	375, 566
Ce ³⁺	gl	0.1 M KCl	20	1.5	2.64	4.27	8.60	10.58	20.40	<3	9
Ce ³⁺	pol	0.1 M KNO ₃	20	20.10	...	252
Ce ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	20.5	...	375, 566
Pr ³⁺	gl	0.1 M KCl	25	1.79	2.56	4.42	8.76	10.42	21.85	...	203
Pr ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	21.07	2.38	375, 566
Nd ³⁺	gl	0.1 M KCl	25	1.79	2.56	4.42	8.76	10.42	22.24	...	203
Nd ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	21.60	2.39	375, 566
Sm ³⁺	gl	0.1 M KCl	25	1.79	2.56	4.42	8.76	10.42	22.84	...	203
Sm ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	22.34	2.20	375, 566
Eu ³⁺	gl	0.1 M KCl	25	1.79	2.56	4.42	8.76	10.42	22.91	...	203
Eu ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	22.39	2.15	375, 566
Gd ³⁺	gl	0.1 M KCl	25	1.79	2.56	4.42	8.76	10.42	23.01	...	203
Gd ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	22.46	2.39	375, 566
Tb ³⁺	gl	0.1 M KCl	25	1.79	2.56	4.42	8.76	10.42	23.21	...	203
Tb ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	22.71	2.14	375, 566
Dy ³⁺	gl	0.1 M KCl	25	1.79	2.56	4.42	8.76	10.42	23.46	...	203
Dy ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	22.82	2.19	375, 566
Ho ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	22.78	2.25	375, 566
Er ³⁺	gl	0.1 M KCl	25	1.79	2.56	4.42	8.76	10.42	23.18	...	203
Er ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	22.74	2.00	375, 566
Tm ³⁺	gl	0.1 M KCl	25	1.79	2.56	4.42	8.76	10.42	22.97	...	203

TABLE II (Continued)

Metal	Method	I	T, °C.	pK of					Log K ₁	Log K ^H _{MHL}	Ref.
				H ₂ L	H ₃ L ⁻	H ₄ L ²⁻	H ₅ L ³⁻	HL ⁴⁻			
Tm ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	22.72	1.90	375, 566
Yb ³⁺	gl	0.1 M KCl	25	1.79	2.56	4.42	8.76	10.42	22.97	2.8	203
Yb ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	22.62	2.30	375, 566
Lu ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	22.44	2.18	375, 566
Y ³⁺	gl	0.1 M KCl	25	1.79	2.56	4.42	8.76	10.42	22.40	...	203
Y ³⁺	Hg	0.1 M KNO ₃	25	4.32	8.53	10.43	22.05	1.91	375, 566

C₁₄H₂₄O₁₀N₂. (HO₂CCH₂)₂NCH₂CH₂OCH₂CH₂OCH₂CH₂N(CH₂CO₂H)₂. 1,2-Bis[2-di(carboxymethyl)aminoethoxy]ethane: HL

Metal	Method	I	T, °C.	pK of				Log K ₁	Ref.
				H ₂ L	H ₃ L ⁻	H ₄ L ²⁻	HL ³⁻		
La ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	15.55	326, 327
La ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	15.84	219, 327
Ce ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	15.70	326, 327
Ce ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	16.06	219, 327
Pr ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	16.05	326, 327
Pr ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	16.17	219, 327
Nd ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	16.28	326, 327
Nd ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	16.59	219, 327
Sm ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	16.88	326, 327
Sm ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.25	219, 327
Eu ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.10	326, 327
Eu ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.77	219, 327
Gd ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	16.94	326, 327
Gd ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.50	219, 327
Tb ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.27	326, 327
Tb ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.80	219, 327
Dy ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.42	326, 327
Dy ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.84	219, 327
Ho ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.38	326, 327
Ho ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.90	326, 327
Er ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.40	326, 327
Er ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	18.00	219, 327
Tm ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.48	326, 327
Tm ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.96	219, 327
Yb ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.78	326, 327
Yb ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	18.22	219, 327
Lu ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.81	326, 327
Lu ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	18.48	219, 327
Y ³⁺	Hg	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	16.82	326, 327
Y ³⁺	pol	0.1 M KNO ₃	20	2.0	2.68	8.85	9.43	17.16	219, 327

^a See ref. 48 and 49 for abbreviations and symbols. ^b The fourth constant could not be obtained accurately. The heavier metals also appear to form very weak binuclear complexes. ^c A fifth complex was indicated but only approximate values could be obtained for the formation constants. ^d Electromigration. ^e If the ligand anion is represented by LOH, then La³⁺ + LO²⁻ → La(LO)₂⁻, log K = 16.82; La³⁺ + 2LO²⁻ + LOH⁻ → La(LO)₂(LOH)²⁻, log K = 16.57. ^f Ln³⁺ + 3HL + 3L⁻ → LnL₃(HL)₃. ^g Since these were determined using the value of K_{CuL⁻} at 29.6°, they are slightly low (455). ^h Values corrected for complexing by acetate buffer.

TABLE III

STABILITY CONSTANTS FOR COMPLEXES OF THE RARE EARTH IONS WITH INORGANIC LIGANDS^a

Metal	Method	T, °C.	Medium	Log of equilibrium constant, remarks		Ref.
				Nitrate, NO ₃ ⁻		
La ³⁺	dist	22	1(HClO ₄)	K ₁ 0.11		427
Ce ³⁺	dist	K ₁ 1.04, K ₂ 0.47		153
Ce ³⁺	dist	22	1(HClO ₄)	K ₁ 0.11		427
Pr ³⁺	dist	22	1(HClO ₄)	K ₁ 0.23		427
Eu ³⁺	dist	22	1(HClO ₄)	K ₁ 0.30		427
Tm ³⁺	dist	22	1(HClO ₄)	K ₁ -0.15		427
Yb ³⁺	dist	22	1(HClO ₄)	K ₁ -0.22		427
Lu ³⁺	dist	22	1(HClO ₄)	K ₁ -0.22		427
Y ³⁺	dist	...	3	K ₁ 0.68-0.33		407
Pyrophosphate, P ₂ O ₇ ⁴⁻						
Y ³⁺	i. ex	25	0.1(NaClO ₄)	β ₂ 9.7		400
Triphosphate, P ₃ O ₁₀ ⁵⁻						
La ³⁺	gl	...	0.1(NaClO ₄)	β ₂ 15.81, HL ⁴⁻ ; K ₁ 4.63, HL ⁴⁻ ; K ₁ K ₂ 8.32		468
Pr ³⁺	gl	...	0.1(NaClO ₄)	β ₂ 16.95, HL ⁴⁻ ; K ₁ 4.86, HL ⁴⁻ ; K ₁ K ₂ 8.64		468
Sm ³⁺	gl	...	0.1(NaClO ₄)	β ₂ 16.98, HL ⁴⁻ ; K ₁ 4.89, HL ⁴⁻ ; K ₁ K ₂ 8.66		468
Eu ³⁺	gl	...	0.1(NaClO ₄)	β ₂ 16.91, HL ⁴⁻ ; K ₁ 4.90, HL ⁴⁻ ; K ₁ K ₂ 8.68		468
Gd ³⁺	gl	...	0.1(NaClO ₄)	β ₂ 16.92, HL ⁴⁻ ; K ₁ 4.91, HL ⁴⁻ ; K ₁ K ₂ 8.72		468
Dy ³⁺	gl	...	0.1(NaClO ₄)	β ₂ 17.12, HL ⁴⁻ ; K ₁ 4.94, HL ⁴⁻ ; K ₁ K ₂ 8.84		468
Er ³⁺	gl	...	0.1(NaClO ₄)	β ₂ 17.41, HL ⁴⁻ ; K ₁ 5.00, HL ⁴⁻ ; K ₁ K ₂ 9.05		468
Yb ³⁺	gl	...	0.1(NaClO ₄)	β ₂ 17.95, HL ⁴⁻ ; K ₁ 5.20, HL ⁴⁻ ; K ₁ K ₂ 9.29		468
Y ³⁺	gl	...	0.1(NaClO ₄)	β ₂ 17.21, HL ⁴⁻ ; K ₁ 4.97, HL ⁴⁻ ; K ₁ K ₂ 8.87		468

TABLE III (Continued)

Metal	Method	T, °C.	Medium	Log of equilibrium constant, remarks	Ref.
Sulfate, SO ₄ ²⁻					
Ce ³⁺	i. ex	25	0.5(NaClO ₄)	K ₁ 1.75, K ₂ 1.15	50
Eu ³⁺	dist	25	0 cor.	K ₁ 3.56	333
Y ³⁺	dist	...	3	K ₁ 2.22, K ₂ 1.08, K ₃ -1.16	407
Fluoride, F ⁻					
Y ³⁺	red	25	0 cor.	K ₁ 4.81, K ₂ 3.73, K ₃ 3.60 (ΔH ₁ = -0.93, ΔS ₁ = -1)	417
Y ³⁺	red	25	0.5(NaClO ₄)	K ₁ 3.88	491
Chloride, Cl ⁻					
La ³⁺	dist	22	1(HClO ₄)	K ₁ 0.05	427
La ³⁺	sol	25	0.5	K ₁ 0.46	514
Ce ³⁺	dist	22	1(HClO ₄)	K ₁ 0.05	427
Pr ³⁺	dist	22	1(HClO ₄)	K ₁ 0.05	427
Sm ³⁺	sol	25	0.5	K ₁ 0.46	514
Eu ³⁺	dist	22	1(HClO ₄)	K ₁ 0.05	427
Tm ³⁺	dist	22	1(HClO ₄)	K ₁ 0.10	427
Yb ³⁺	dist	22	1(HClO ₄)	K ₁ 0.22	427
Yb ³⁺	sol	25	0.5	K ₁ 0.56	514
Lu ³⁺	dist	22	1(HClO ₄)	K ₁ 0.40	427
Lu ³⁺	sol	25	0.5	K ₁ 0.48	514
Y ³⁺	dist	...	3	K ₁ 0.89-0.13	407
Y ³⁺	red	15-35	0 cor.	K ₁ 0.38 (15°), 0.36 (25°), 0.32 (35°) (ΔH ₁ = -0.3, ΔS ₁ = -1)	416
Bromide, Br ⁻					
Y ³⁺	red	15-35	0 cor.	K ₁ 0.49 (15°), 0.40 (35°) K ₁ 0.45 (25°) (ΔH ₁ = -0.9, ΔS ₁ = -1)	416

^a See ref. 48 and 49 for abbreviations and symbols.

Indeed, this is the coordination number that has been assumed by many authors. Although this assumption may be valid for some species, there is an increasingly impressive array of evidence that the true coordination number is larger than six (222). The following experimental observations are significant in this respect:

1. Many solid salts contain more than six molecules of water per cation. The crystal structures of these compounds, where determined, invariably indicate higher coordination numbers. Thus, the solid compounds Ln(BrO₃)₃·9H₂O (213, 485, 510), Ln₂(SO₄)₃·9H₂O (244), Ln(C₂H₅OSO₃)₃·9H₂O (151, 272, 510), and probably Ln₂(SO₄)₃·8H₂O (171, 510) all contain the grouping Ln(H₂O)₉³⁺, which has a trigonal prismatic geometry with three water molecules opposite the rectangular faces. A second form of Ln₂(SO₄)₃·9H₂O (347) contains the grouping Ln(H₂O)₆O₃⁹⁻, which amounts to two interpenetrating trigonal prisms and requires a coordination number of twelve.

2. The crystals of some 6-hydrates do not contain the grouping Ln(H₂O)₆³⁺. Thus, the compound GdCl₃·6H₂O (335), and presumably other isomorphous salts of this composition, includes the grouping Gd(H₂O)₆Cl₂⁺, a square antiprismatic arrangement of coordination number eight.

3. The removal of water from the solid species Ln(diket)₃·H₂O results in their destruction (451). This

ubiquitous water molecule is most probably bonded to the Ln³⁺ ion, suggesting seven-coordination (222).

4. The formation of Ln(diket)₄⁻ as the piperidine salts (620a) requires a coordination number of at least eight.

5. The formation of complex ions such as Ln(RCH(OHCO₂)₄)⁻ (85, 235a), Ln(cit)_n⁽³⁻³ⁿ⁾ (24, 51, 314, 471, 492), Ln(NTA)₂³⁻ (8, 365), Ln(DTPA)₂⁻ (203, 375), Ln(HEDTA)(IMDA)₂⁻ (569), and Ln(gluc)₂²⁺ (295, 296), where more than six donor sites exist for each Ln³⁺ ion, probably requires coordination numbers in excess of six.

6. The ability of certain complex species to add additional ligands, *e.g.*, to form Ln(HEDTA)(IMDA)₂⁻ (569), Ln(NTA)₂⁻ (8, 365), or Ln(HEDTA)(OH)⁻ (198, 570) again indicates coordination numbers larger than six.

7. The existence of the species HLn(EDTA)(H₂O)_n and Ln(EDTA)(H₂O)_m⁻ (67, 221, 287, 363, 372) and the commonness with which water appears in the derivatives of the other polyaminepolycarboxylates (32, 368) require a larger coordination number than six.

8. The commonness of the LnF₇³⁻ composition in the solid fluoro derivatives of the tetrapositive ions (13, 15, 238-241) indicates, but does not require, a coordination number of seven.

9. The crystal structures of a number of compounds

that are not complexes indicate clearly that irrespective of oxidation state these cations are most commonly associated with 7-12 nearest donor neighbors.

The problem of coordination number can best be solved by determination of the crystal structures of representative complex species. A promising beginning indicates ten-coordination in the compound $\text{HLa}(\text{EDTA})(\text{H}_2\text{O})_4 \cdot 3\text{H}_2\text{O}$ and nine-coordination in the ion $\text{La}(\text{EDTA})(\text{H}_2\text{O})_3^-$ (221).

III. FORMATION AND STABILITY OF COMPLEX SPECIES IN SOLUTION

A. EXPERIMENTAL TECHNIQUES FOR DETECTING SUCH SPECIES

The experimental techniques that have been used to determine the existence of complex species in solutions containing the rare earth metal ions have been discussed previously (360, 545, 565) and are not considered here.

B. STABILITIES

1. Evaluation of Formation Constants

Values for the formation constants of rare earth complexes have been determined by a variety of experimental and computational techniques. All of these have been discussed and critically evaluated in a recent treatise (470).

2. Formation-Constant Data

The values of the formation constants for the rare earth complexes which have been investigated since 1955 for organic ligands and 1956 for inorganic ligands are given in Tables II and III, respectively. Earlier work has been tabulated previously (48, 49) and since these volumes set the pattern for recording formation-constant data, this format has been followed, using the same notation and set of symbols. The only difference is that because this paper is concerned only with the rare earths, the metal ions are listed in order of increasing atomic number rather than alphabetically.

It is very difficult to assess the relative precision and accuracy of formation-constant data. For this reason there are often several determinations for the same system given in the tables. In a few cases in which the values are obviously incorrect, they have been omitted, and in a few others a question mark is used to signify that the number appears to be in doubt.

3. Interpretation of Trends in Formation-Constant Data

A complete discussion of the trends in the formation-constant data for rare earth metal complexes is severely limited by the fact that only seventeen ligands have been studied with all the rare earth ions. (Since the

formation constant of only the EDTA complex of promethium has been determined, promethium will be omitted in this discussion.) Data for these ligands that have been studied completely indicate that it is not permissible to interpolate or extrapolate in systems where only a few of the rare earth metal ions have been studied (566). Consequently, although there is now a rather large collection of formation constants for rare earth complexes which is useful and interesting, only a very small proportion of these data can be used in the type of comparison which is presented here.

Since there is a regular decrease in the crystal radii of the rare earth metal ions, simple electrostatic theory and the abundance of data suggesting that these ions form predominantly ionic complexes (see section IV) predict a direct relationship between the atomic number of the rare earth metal ion and the magnitude of the formation constant (191, 192, 263a, 376). In nearly all complexes which have been studied, this is precisely what is found for the values of $\log K_1$ for complexes of the light rare earths, lanthanum through europium. [There are a few ligands for which the europium complex is less stable than the samarium complex (85, 89, 187, 285, 319, 364, 365, 455, 532).] This simple relationship is, however, not generally found when the heavy rare earth metal ions, terbium to lutetium, are considered.

The trends in the formation constant data for the elements heavier than gadolinium can be divided qualitatively into three types. The first group contains those ligands for which there is a regular increase in the formation constants. This does not imply that these ligands follow the simple electrostatic model, since the slope of the plot of $\log K_1$ vs. $1/r$ (r = radius of the ion) is usually not the same as for the light earths. Ligands for which this trend is observed are glycolic acid (85, 89, 269, 519), lactic acid (85, 89, 269), iminodiacetic acid (203, 567), α -hydroxyisobutyric acid (85, 89, 285), nitrilotriacetic acid (319, 365), ethylenediamine- N,N' -diacetic acid (568), ethylenediamine- N,N,N',N' -tetraacetic acid (487, 622), 1,2-diaminocyclohexane- N,N,N',N' -tetraacetic acid (269, 369, 487), and [2-di(carboxymethyl)aminoethoxy]ethane (219, 326, 327) (this ligand might also be placed in the second group). The only obvious similarity among these ligands is that each is capable of forming at least one chelate ring in the complexes.

The ligands in the second classification form complexes for which the formation constants of the heavy earths have very nearly the same values from gadolinium to lutetium. These ligands are acetic acid (285, 286, 517, 518), mercaptoacetic acid (29, 285), methoxyacetic acid (285), acetylacetone (191), dipicolinic acid (187), and N' (2-hydroxyethyl)ethylenediamine- N,N,N' -tri-acetic acid (364, 455, 532). The last three ligands show a slight upward trend in the $\log K_1$ values near the

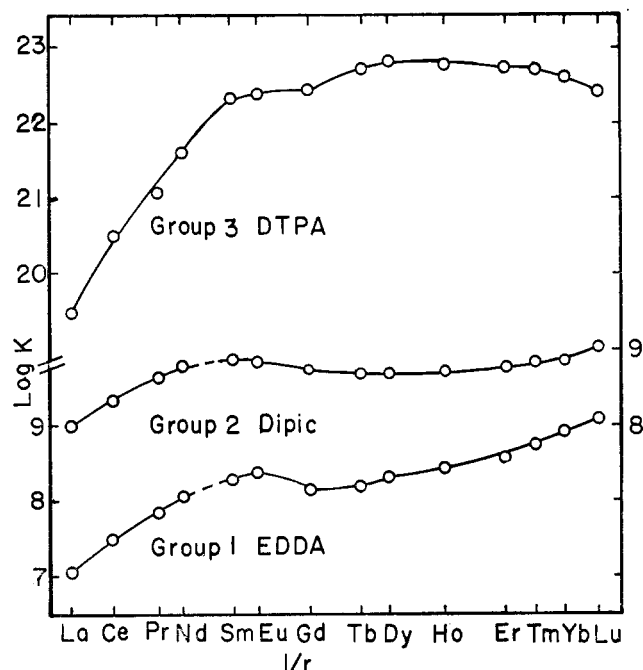


Figure 1—Typical plots of formation constants of rare earth complexes against the reciprocal of the ionic radius of the rare earth ion (the numbers on the left refer to groups 1 and 3; the numbers on the right refer to group 2).

end of the series. Again it is difficult to see any distinct relationship.

The third group contains only two examples at present, 2,2'-bis[di(carboxymethyl)amino]diethyl ether (219, 326, 327) and diethylenetriamine-*N,N,N',N',N''*-pentaacetic acid (203, 375, 566). The formation constants for the complexes of these two ligands increase with the first elements beyond gadolinium and then show a slight decrease to lutetium. Illustrative examples of these three groups are presented in Figure 1.

For all ligands which have been studied, the gadolinium complex is less stable than would be expected from the simple electrostatic model. This behavior has been called the "gadolinium break" and cannot be explained, as was originally attempted (622), by assuming a steric effect, since it is still apparent in ligands for which there should be no steric interference (486a).

The position of yttrium with respect to the magnitude of the formation constants of its complexes is of interest. On the basis of the simple electrostatic model, yttrium should be positioned between holmium and thulium. That such is not the case has been clearly recognized (192, 376). An examination of the data in Table II shows that it is possible to make some general observations concerning the position of yttrium. If the magnitude of the formation constants of the yttrium complexes of the ligands mentioned in the first group are considered, it is apparent that yttrium is similar to the heavy rare earths. In some cases, there is confusion as to the relative position owing to the fact

that different workers find slightly different values for the formation constants (*e.g.*, see the glycolic acid complexes). Of the other two exceptions, it was pointed out earlier that [2-di(carboxymethyl)aminoethoxy]ethane might possibly be classified in the second group. The only ligand for which no rationalization is apparent is ethylenediamine-*N,N'*-diacetic acid (568).

In the second group, yttrium is always found among the light rare earths, and with three ligands, acetic acid (285, 286, 521), methoxyacetic acid (285), and mercaptoacetic acid (285), the yttrium ion has the smallest formation constant for any of the cations. For the two members of the third group, yttrium is also found in the light rare earth region.

The trends in the formation constants of the 2:1 and higher complexes are much more difficult to systematize since in many of these species there is good evidence for assuming that steric effects are important, and also, for the simple complexes, the errors in the measurements are so large that it is difficult to decide which trends are real. When it is possible to make a selection, it is generally found that the ligands remain in the same groups as previously. The most notable exception is dipicolinic acid, which appears in the first group on the basis of its $\log K_2$ values (187).

The position of yttrium is quite interesting in the 2:1 complexes because it can be completely shifted from its position in the 1:1 series. For example, yttrium would be in the heavy earth region in the 2:1 complexes with mercaptoacetic acid (285) and methoxyacetic acid (285). In the iminodiacetic acid species (567), it has shifted into the light earth region, and with acetylacetonone (191), the 2:1 yttrium chelate has the largest formation constant of all.

The interpretation of the trends which have been noted is difficult and at most only partly satisfactory. Without a doubt, the rare earth metal ions coordinate predominantly to oxygen donors (486). Very little work has been done with nitrogen donors, since the basicity of most of these compounds is such that rare earth metal hydroxides precipitate before coordination occurs (486). The only reported work using sulfur as a donor atom (29, 79, 188, 285, 574) seems to indicate that the sulfur atom coordinates very weakly, if at all, to these ions.¹

Effectively, there are three considerations which have been evoked to aid in explaining these trends. None of these is very satisfactory, but each is briefly outlined below and its strength and weakness pointed out.

The possible existence of crystal-field effects in rare earth metal chelates (85, 538) is attractive for those ligands in the first group since the change in the $\log K_1$ values with increasing atomic number is reminiscent of the trend noted among the d-type transition elements.

(1) The reported observation that thiodiglycolic acid coordinates more strongly than diglycolic acid is incorrect (190).

Of particular significance is the fact that there is a break at the gadolinium ion, for which there should be no crystal-field stabilization. Moreover, since the yttrium ion also has no crystal-field stabilization, crystal-field effects could explain why the yttrium chelates do not quite fall in the expected region based on the radius of the yttrium ion. An estimate of the crystal-field stabilization in the holmium and dysprosium complexes of α -hydroxyisobutyric acid has been made on this basis (85). Since both gadolinium and yttrium have zero crystal-field stabilization, it would be expected on the basis of size that the yttrium complex of a given ligand would always be more stable than the gadolinium complex. Such is not the case. In addition, it has been pointed out that such structurally similar ligands as ethylenediamine- N,N,N',N' -tetraacetic acid and N' -(2-hydroxyethyl)ethylenediamine- N,N,N' -triacetic acid are not amenable to this type of explanation if the heavy rare earth ions are considered (470). Moreover, when the ligands of the second group are considered, the crystal-field modification of the electrostatic argument does not hold since there is no regular increase in the $\log K_1$ values.

The second consideration which has been advanced is concerned with the possible existence of a coordination number greater than six, the value which has usually been assumed. Evidence for this expanded coordination number has been obtained from those systems which have more than six donor atoms (section II). The formation constants of the rare earth diethylenetriaminepentaacetic acid chelates (203, 375) are larger than the formation constants of the ethylenediaminetetraacetic acid chelates (487, 622), and this incremental increase is much larger than for any other metal ion which has been studied. These observations suggest that the coordination number of the rare earth ion is larger than six (9). Similar arguments have been presented for the 2:1 complexes with nitrilotriacetic acid (8) and ethylenediamine- N,N' -diacetic acid (568). It has also been suggested that the rare earth metal ion in the ethylenediaminetetraacetic acid chelates and in the acetylacetonate chelates is seven-coordinate with a water molecule occupying the seventh position (222). Both nine- and ten-coordination have been described for the ethylenediaminetetraacetic acid chelates (221). The existence of negative rare earth species with α -hydroxycarboxylic acids can be explained either with a coordination number greater than six or by assuming that two ligands are bound through only one donor atom (85, 89).

The third consideration which has been used is the existence of steric factors, both for cases in which the larger coordination number is presumed and for cases for which the octahedral configuration is presumed. Steric factors are undoubtedly important in the decrease of the values of $\log K_2$ for the nitrilotriacetic acid com-

plexes of the rare earths heavier than dysprosium (8), although the increase at lutetium is unexplained (365). Likewise, steric factors can be invoked to explain the similar effect in the diethylenetriaminepentaacetic acid (203, 375, 566) and 2,2'-bis[di(carboxymethyl)-amino]diethyl ether chelates (219, 326, 327). Steric effects arise in the former owing to the large number of donor groups and in the latter because of the inability of the ligand to adapt to the smaller metal ions.

Steric hindrance is also evident in the values of $\log K_3$ for dipicolinic acid (187, 192), but it is difficult to explain the regular increase in the $\log K_2$ values as compared to the decreasing values in the middle portion of the $\log K_1$ values. For simple ligands, steric effects have been postulated only for methoxyacetic acid (285), and it has been shown that for some α -methyl- α -hydroxycarboxylic acids inductive effects are more important than possible steric effects (85, 89).

4. Thermodynamic Considerations

The unsatisfactory state of affairs with regard to the interpretation of the trends in the rare earth formation-constant data has led a number of workers to examine the thermodynamics of the formation of some of these species in aqueous solution. The data which have been obtained are listed in Table IV.

Since the only complete studies have been with the aminopolycarboxylic acids, only this type of ligand can be discussed. The first study of this kind used ethylenediaminetetraacetic acid as the ligand (44), and the results indicated that the complexes could be divided into two groups at gadolinium on the basis of the magnitude of $\Delta S^\circ + \bar{S}^\circ_{Ln^{3+}}$, where ΔS° is the entropy of chelate formation and $\bar{S}^\circ_{Ln^{3+}}$ is the partial molal entropy of the free rare earth metal ion. This sum is equivalent to the partial molal entropy of the chelate, \bar{S}°_{LnY} (with an additive constant, the partial molal entropy of the ligand anion). The difference between the two groups was explained by a unit change in multidentate character of the ligand at gadolinium. The possibility that the coordination number of the cation may change at this point cannot be excluded (221). (The values of ΔH_1 obtained in this study are not reported since it has been shown that the absolute values are incorrect (43).)

A study of molecular models did not support this abrupt change in the number of donor groups utilized (538), and new data which have been obtained from calorimetric measurements on this system (328) do not show such an abrupt change although the ions can still be divided into two groups on the basis of the values of \bar{S}°_{LnY} .

That the simple electrostatic model is not completely satisfactory is indicated by the fact that the ΔH° values in the heavy rare earth region are smaller than in the

TABLE IV
HEATS AND ENTROPIES OF FORMATION OF RARE EARTH COMPLEXES

Metal	ΔH_f° , kcal./mole	ΔS_f° , e.u./mole	$\Delta S_f^\circ + \bar{S}^\circ_{Ln}$, e.u./mole	Ref.
Glycolic Acid				
Ce ³⁺	-0.44	8.9	-27	85, 89
Gd ³⁺	-0.40	9.9	-32	85, 89
Malonic Acid				
La ³⁺	4.8	39	4	173
Gd ³⁺	5.1	42	0	173
Lu ³⁺	5.2	44	-4	173
Lactic Acid				
Ce ³⁺	-0.83	7.9	-28	85, 89
Gd ³⁺	-0.54	9.8	-32	85, 89
α -Hydroxyisobutyric Acid				
Ce ³⁺	-0.83	8.4	-28	85, 89
Gd ³⁺	-0.89	9.9	-32	85, 89
Ethylenediamine-N,N,N',N'-tetraacetic Acid				
La ³⁺	-2.93	59.7	25	328
La ³⁺	-4.1	53	18	642
Ce ³⁺	-2.94	60.8	25	328
Ce ³⁺	-2.43	64.8	29	538
Pr ³⁺	-3.20	61.4	24	328
Nd ³⁺	-3.62	61.3	23	328
Nd ³⁺	-2.98	65.8	27	538
Sm ³⁺	-3.35	64.4	24	328
Eu ³⁺	-2.56	67.6	27	328
Gd ³⁺	-1.73	71.2	29	328
Gd ³⁺	-1.11	75.7	34	538
Tb ³⁺	-1.11	75.5	33	328
Dy ³⁺	-1.21	77.3	34	328
Ho ³⁺	-1.36	78.0	34	328
Er ³⁺	-1.71	78.3	33	328
Tm ³⁺	-1.87	79.1	33	328
Yb ³⁺	-2.31	79.2	32	328
Lu ³⁺	-2.51	79.1	32	328
Y ³⁺	-0.59	77.5	30	328
Y ³⁺	+0.32	83.8	37	538
N'-(2-Hydroxyethyl)ethylenediamine-N,N,N'-triacetic Acid				
La ³⁺	-2.20	54.2	20	364
Ce ³⁺	-3.06	54.4	18	364
Pr ³⁺	-4.45	52.0	15	364
Nd ³⁺	-4.25	53.8	15	364
Sm ³⁺	-4.65	54.4	16	364
Eu ³⁺	-4.81	54.1	13	364
Gd ³⁺	-4.66	54.1	12	364
Tb ³⁺	-3.39	58.8	16	364
Dy ³⁺	-2.12	62.8	19	364
Ho ³⁺	-1.14	66.3	22	364
Er ³⁺	-0.32	69.4	24	364
Tm ³⁺	0.92	74.5	29	364
Yb ³⁺	0.36	74.0	27	364
Lu ³⁺	0.22	73.4	26	364
Y ³⁺	-0.29	66.1	19	364
1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic Acid				
La ³⁺	3.55	86.7	52	369
Pr ³⁺	5.00	95.6	58	369
Nd ³⁺	5.00	97.6	59	369
Sm ³⁺	5.00	102.00	62	369
Eu ³⁺	5.54	104.5	63	369
Gd ³⁺	5.75	105.3	64	369
Tb ³⁺	5.00	105.1	62	369

TABLE IV (Continued)

Metal	ΔH_1° , kcal./mole	ΔS_1° , e.u./mole	$\Delta S_1^\circ + \bar{S}^\circ_{Ln}$, e.u./mole	Ref.			
Dy ³⁺	3.09	100.5	57	369			
Ho ³⁺	1.18	95.0	51	369			
Er ³⁺	0.12	92.8	48	369			
Tm ³⁺	-1.59	88.3	42	369			
Yb ³⁺	-4.49	80.2	33	369			
Lu ³⁺	-4.92	79.2	32	369			
Y ³⁺	4.23	103.0	56	369			
Diethylenetriamine-N,N,N',N',N''-pentaacetic Acid							
La ³⁺	-5.7	70.0	35	375, 376			
Pr ³⁺	-7.1	72.0	35	375, 376			
Nd ³⁺	-5.8	79.4	41	375, 376			
Sm ³⁺	-8.2	74.7	34	375, 376			
Eu ³⁺	-8.1	75.3	34	375, 376			
Gd ³⁺	-7.5	77.6	36	375, 376			
Tb ³⁺	-7.7	78.1	36	375, 376			
Dy ³⁺	-8.0	77.6	34	375, 376			
Ho ³⁺	-7.6	78.7	34	375, 376			
Er ³⁺	-7.3	79.6	34	375, 376			
Tm ³⁺	-5.5	85.5	39	375, 376			
Yb ³⁺	-5.5	85.1	38	375, 376			
Lu ³⁺	-4.6	87.2	41	375, 376			
Y ³⁺	-5.2	83.4	36	375, 376			
Nitrilotriacetic Acid							
Metal	ΔH_1° , kcal./mole	ΔH_2° , kcal./mole	ΔS_1° , e.u./mole	$\Delta S_1^\circ + \bar{S}^\circ_{Ln}$, e.u./mole	ΔS_2° , e.u./mole	$\Delta S_1^\circ + \Delta S_2^\circ + \bar{S}^\circ_{Ln}$, e.u./mole	Ref.
La ³⁺	2.05	-2.43	54.3	20	25.0	45	365
Ce ³⁺	1.25	-3.06	53.8	18	25.6	43	365
Pr ³⁺	0.45	-3.72	52.2	15	24.9	40	365
Nd ³⁺	0.68	-3.78	53.8	15	26.1	41	365
Sm ³⁺	0.40	-4.37	54.1	14	26.5	40	365
Eu ³⁺	0.93	-5.08	55.8	15	25.0	40	365
Gd ³⁺	1.02	-5.80	56.2	14	22.9	37	365
Tb ³⁺	1.71	-5.21	58.8	16	25.4	42	365
Dy ³⁺	2.25	-5.61	61.3	18	24.2	42	365
Ho ³⁺	2.63	-5.15	63.3	19	25.5	44	365
Er ³⁺	2.51	-3.87	63.5	18	29.4	48	365
Tm ³⁺	1.90	-2.36	62.3	16	34.3	51	365
Yb ³⁺	2.09	-1.86	63.7	17	36.3	53	365
Lu ³⁺	1.98	-1.11	63.8	16	39.4	56	365
Y ³⁺	2.69	-4.19	61.6	15	26.9	42	365

light region. If crystal-field stabilization were the dominating factor, ΔH° for the gadolinium chelate should be less than for the heavier chelates. Since this is not the case, it can be concluded that the "gadolinium break" is not due predominantly to crystal-field effects. That other factors are important is obvious, but the nature of these factors is not clear at present. Some possible factors are discussed in the next paragraphs.

The chelates of the ligands, nitrilotriacetic acid (365), N'-(2-hydroxyethyl)ethylenediamine-N,N,N'-triacetic acid (364), diethylenetriaminepentaacetic acid (375, 566), and 1,2-diaminocyclohexanetetraacetic acid (369) exhibit approximately the same trends in ΔH° values as do the ethylenediaminetetraacetic acid chelates; namely, the chelates can be divided, rather roughly, into two groups, one before gadolinium and one after gadolinium. The trends within these groups again make it difficult to rationalize in terms of crystal-field effects. The low values of the enthalpy of formation of

these species indicate that entropy effects are predominant in determining stability. The trends in the enthalpy values can be treated in a manner similar to the entropy values (see below).

The entropy values for the formation of these chelates are quite large. In all cases it is again possible to divide the \bar{S}°_{LnY} values into two groups, with gadolinium as the dividing point. It is not possible, however, to attribute this to a sudden change in coordination requirements. Rather there appears to be a contribution both from translational and configurational changes (364). The latter are due to the effects of such properties of the rare earth metal ion as electronic configuration, charge, size, and mass on the internal degrees of freedom of the ligand. Since the available evidence is against an abrupt change in structure (328, 538), the translational component of the entropy change should be less significant than the changes due to gradual increase in bond strength and steric hindrance as the ionic radius decreases. This combined effect should re-

sult in gradual loosening of the bonds and an increase in the configurational entropy as is generally observed. It is somewhat more difficult to rationalize the values for the 1,2-diaminocyclohexanetetraacetic acid chelates (369) in this manner, but it should be borne in mind that this ligand has more rigid chelating requirements because of its structure.

The position of yttrium, on the basis of the enthalpy and entropy values of the chelates discussed here, is always near holmium. The fact that the formation constants for yttrium chelates lie in the cerium earth region in some cases reflects those minor factors other than ionic size (such as mass and electronic configuration) which affect the enthalpy and entropy values to different degrees depending upon the particular ligand (364).

It is appropriate at this point to reiterate that the only thermodynamic data which are available are concerned with rather complicated ligands, and there is essentially no background on the properties of simpler compounds on which to build. In order to obtain a satisfactory explanation for the properties of these materials, it will be necessary to obtain accurate data for the simpler compounds. Studies of this type are now in progress in a number of laboratories.

IV. BONDING IN COMPLEX SPECIES

A. PHYSICAL DATA AND THEIR INTERPRETATION

1. Magnetic Data

The magnetic susceptibilities of the 1:1 chelates of neodymium with ethylenediamine-*N,N,N',N'*-tetraacetic acid, 1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid, 2,2'-bis[di(carboxymethyl)amino]diethyl ether, 1,2-bis[2-di(carboxymethyl)aminoethoxy]ethane, diethylenetriamine-*N,N,N',N',N''*-pentaacetic acid, and *o*-phenylenediamine-*N,N,N',N'*-tetraacetic acid have been reported (225, 233). In addition, Holleck and Sölla (234) have measured the magnetic susceptibilities of the 1:1 chelates formed by the ligands named above with erbium. As compared with the paramagnetism of the lanthanide trivalent ion in $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, the molar susceptibility decreases as the stability constant of the complex in aqueous solution increases, following a linear relationship when χ_M is plotted against $\log K$ for all experimental values, except for those for the chelates with 2,2'-bis[di(carboxymethyl)amino]diethyl ether and 1,2-bis[2-di(carboxymethyl)aminoethoxy]ethane. Identical results are obtained when χ_M is plotted *vs.* $\log K$ for the erbium compounds, with the same two discrepancies as before. Linearity between χ_M and $\log K$ was interpreted as due to an increase in the percentage of covalency in the metal ion to donor-group bond, which would affect the 4f electrons. However, it should be pointed out that some of the values of $\log K$ used in the plots do not agree with other reported data

(327, 375, 622). Lack of involvement of 4f electrons in the bonding under discussion was suggested by the observation that the molar susceptibilities, at room temperature, of the 1:1 chelates formed by ethylenediamine-*N,N,N',N'*-tetraacetic acid, *N'*-(2-hydroxyethyl)ethylenediamine-*N,N,N'*-triacetic acid, and 1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid with tripositive praseodymium, neodymium, samarium, europium, and gadolinium (368) agree, within experimental error, with the corresponding susceptibilities of the 8-hydrated sulfates (646). The latter, in turn, agree with the theoretical values for the free gaseous ions (586, 587).

The magnetic susceptibilities of some of the chelates with acetylacetone and ethylenediamine-*N,N,N',N'*-tetraacetic acid, over the temperature range 1.3–20°K., have been reported recently (162). However, the theoretical treatment of these results (161) has little bearing upon the nature of the bond between the metal ion and the chelating ligand, since it assumes that the paramagnetic ions are in sites of cubic symmetry with octahedral coordination about the ion, although it seems probable that the actual structure has a somewhat lower symmetry and higher coordination. It is significant that, although the substances in question are coordination compounds, the treatment is comparable to that used for substances that are salts, *e.g.*, the rare earth ethyl sulfates (133). This situation is in keeping with the fact that 4f electrons are not affected by the formation of new bonds in the process of chelation, although they are affected by the symmetry of the surrounding fields.

Proton nuclear magnetic resonance spectra of a number of hydrated cations in aqueous solution have been reported (20). When the logarithms of the acidity constants of the hydrated cations are plotted against the molar shift, most of the experimental values lie along a straight line. This linearity was considered as a confirmation of ion-dipole electrostatic bonding between cations and water molecules. The tripositive lanthanum ion also shows this behavior. However, measurement of the oxygen-17 nuclear magnetic resonance shifts in aqueous solution of all the tripositive ions except promethium (318) suggested that the 6s orbital in the lanthanide ions takes part in the formation of covalent bonds with water molecules.

2. Spectral Data

a. Visible and Ultraviolet

The line-like absorption spectra of rare earth metal compounds arise from electronic transitions within the 4f levels (646). These transitions occur after the removal of degeneracy in the 4f orbitals by external crystal fields. However, this situation is not the same as with d-transition elements, where the absorption

spectra are also due to splitting of previously degenerated levels (d levels in this case). The d electrons, being external in ions of the transition metals, take an active part in bonding, and a change in the environment of the central metal ion frequently causes a substantial variation in the absorption spectra, with substitution for previously existing bands by entirely new ones. Shielding of the 4f electrons by a complete $5s^25p^6$ octet makes such effects less drastic in the lanthanide series.

If we compare the absorption spectra of a variety of rare earth complexes with those obtained from dilute aqueous solutions of lanthanide ions, three general effects are distinguishable, which are thought to be the result of superimposing fields of differing strength around the lanthanide ion. These effects are observed to a different degree in the individual bands of the spectrum. First, there are small shifts, most commonly toward longer wave lengths, although cases of "blue shift" are also reported. Another change consists of splitting of certain of the bands into several small maxima. Finally there is a variation in the specific absorptivity of an individual peak. This general behavior holds for spectra obtained under a wide variety of experimental conditions.

Ephraim (134-140) measured the reflection and absorption spectra of several salts, solid or in solution, of praseodymium, neodymium, and samarium. Similar data were reported by Boulanger (57). Included in Ephraim's work were acetylacetonate chelates, and in that of Boulanger, dibenzoylmethane, ethylenediamine-N,N,N',N'-tetraacetic acid, and nitrilotriacetic chelates. Data for fused systems, consisting of rare earth metal salts dissolved in low-melting eutectics or salts, have been reported (23, 78, 196, 647). Absorption spectra for other media include phosphate glasses (601), water-formamide mixtures (207), and nonaqueous solutions (366, 370, 377, 462).

The most abundant data come, of course, from spectrophotometric studies on aqueous solution. In some instances, the species formed under these conditions are well characterized, and their stability constants have been determined by independent means (potentiometric titration, ion exchange, solvent extraction). It is observed that association of a lanthanide ion with other species causes band shifts, band splittings, and absorptivity changes. This has been confirmed for systems containing ethylenediamine-N,N,N',N'-tetraacetate ions (363, 593) and other chelating agents (226-229). However, when the lanthanide ions are in the presence of species that cannot be expected to associate strongly, the spectra remain unchanged. Thus, the absorption spectrum of promethium ion was found to be the same in both chloride and nitrate solutions (412), and the ultraviolet spectrum of gadolinium ion was found to be substantially identical for both chloride and nitrate

solutions (371). The same general observation has been made for the spectra of several lanthanide ions in chloride, nitrate, and perchlorate solutions, but a red shift of some of the bands was observed in the presence of acetate ions (362).

These results indicate that interaction of the lanthanide ions with other ions in solution can be ascertained from observed changes in the spectra. However, this approach should be considered to be, at most, of only qualitative value, since no absolute correlations can be established between variations in the spectra and stability constants as determined by independent means (368, 599, 600).

Spectrophotometric studies on interaction of rare earth metal ions with other species include anions such as perchlorate (212, 302, 555), nitrate (28), pyrophosphate and sulfate (563), chromate (576), sulfite (597), carbonate (447), acetate (518), citrate, lactate, trihydroxyglutarate, and ethylenediamine-N,N,N',N'-tetraacetate (193, 431), nitrilotriacetate (17), hydrazine-N,N'-diacetate (595), and bis(N,N'-acetylacetylonylidene)ethylenediamine (16). The quantitative conclusions that were drawn from some of these absorption data should be regarded with caution. Since, even upon formation of the strongest complexes, no new bands appear, calculations are based on changes in the intensities of previously existing bands. However, it is often difficult to separate variations due to the formation of new species from changes caused by environmental effects (393). Only when a large change in absorptivity is produced by a relatively small concentration of "ligand" can the results be trusted. Besides, there are many cases in which the stoichiometry of the compound is assumed, without experimental support, in order to calculate its stability constant. This is particularly true for "complexes" of the ion-pair type.

The usefulness of absorption spectrum analysis to ascertain the nature of the bond between the central lanthanide ion and the ligand donor groups is limited. Inasmuch as the observed characteristic bands are due to transitions within the 4f levels, levels that are but little affected by changes in environment, the absorption spectra are substantially identical whether the ion is solvated or associated with chelating agents.

The small splittings of the characteristic absorption bands are undoubtedly due to the effect of crystal fields upon the J levels of the central ion, as happens with the d-transition metals (42, 329). The slight shifts in the bands have been attributed by Jørgensen (264, 266) to the effect of these crystal fields upon certain parameters related to the interelectronic repulsion among the 4f electrons. This effect is also operative in the d-transition series, where the shifts are more pronounced. For example, the shift for manganese complexes can reach 20% of the wave number (given in cm.^{-1}), whereas for the rare earth metal species the change amounts to a

few per cent. Here again shielding by the $5s^25p^6$ octet is of importance.

Pominov (450) has studied the absorption spectra of anhydrous neodymium chloride solutions in water-ethanol mixtures. From the amount of water required to displace ethanol from the solvation layer, he concluded that the solvation energy in ethanol is slightly larger than the corresponding value in water. A similar investigation (359) with anhydrous chromous, cupric, and neodymium chlorides indicated that the maximum hydration coordination number is six for all three cations. It is significant that the electron-transfer spectra of ethanolic solutions of the tripositive cations containing ammonium bromide do indicate some covalent bonding (267). On the other hand, the spectra of aqueous solutions containing tripositive cerium, praseodymium, and neodymium ions, when compared with similar spectra of solutions of heavy metals salts, indicate that no covalent bond is formed between the lanthanide ion and other species existing in solution (75).

b. Infrared

Reported infrared studies relating to the coordination chemistry of rare earths are limited to solid compounds containing chelating ligands. Data reported pertain to the nature of the metal-donor group bond and to the number of donor groups from a given ligand that are attached to the central ion. Comparison of the infrared spectra of ethylenediamine- N,N,N',N' -tetraacetic acid, the monobasic acid, the monobasic acid formed by its 1:1 chelate with neodymium, and the sodium salt of this acid indicates that, in the solid neodymium chelate, one of the carboxylic acid groups remains uncomplexed (372). To explain the observed behavior on ion-exchange resins, it was assumed that the heavier tripositive lanthanide ions form 1:1 chelates with ethylenediaminetetraacetic acid in which the ligand is either quadri- or quinquedentate (604). However, no conclusive evidence for the existence of uncomplexed carboxylate groups could be obtained from the infrared spectra of the complexes $H[Ln(EDTA)] \cdot xH_2O$ for $Ln = Nd, Sm, Ho,$ and Er (604). An extension of the previously cited observations (372) on the infrared spectrum of $H[Nd(EDTA)] \cdot xH_2O$ to other ions in the lanthanide series suggested the existence of a free $-COOH$ group in $Ce(III)$ - $Sm(III)$ compounds (287). For the chelates of europium and the heavier tripositive ions, the peak assigned to the free $-COOH$ group disappears, thus indicating that the ligand becomes sexadentate (287). These conclusions are supported by the observation that, when dried in the oven at 110° over a 24-hr. period, chelates from cerium to samarium retain a water molecule which cannot be removed without decomposition, whereas the chelates of the heavier ions are completely dehydrated. A change from quinqu-

to sexadentate behavior is not reflected in a break of the acidity constants, thus indicating that the solid compounds may differ from the chelates in solution.

Comparisons of the infrared spectra of ethylenediamine- N,N,N',N' -tetraacetic acid complexes of a number of metal ions indicate the bonding between carboxylate groups and the central ion to be primarily ionic in the $Ce(III)$ compound. Weakness in the bonding was also shown by infrared data, in the case of rare earth acetylacetonates (107, 313, 620). Other infrared research includes oxine chelates (436), 4-hydroxybenzothiazole chelates (143), and a compound of cerous ion with bis(2-ethylhexyl)phosphoric acid (421).

3. Structural Data

The only published X-ray crystal structure determinations are for cerium(IV) species. The tetrakis(acetylacetonate), like the corresponding thorium, zirconium, and uranium(IV) compounds, has a square antiprismatic arrangement of eight oxygen atoms about the central cation (185). The same structure is reported for the comparable tetrakis(dibenzoylmethane) complexes (627).

An X-ray study of erbium chloride and iodide in aqueous solution indicated the presence of six water molecules arranged octahedrally around the cation but suggested that the cation interaction with water molecules goes beyond this first layer (58). Indeed, there is a compressed "ice-like" structure in the vicinity of the metal ion, so that the introduction of the free gaseous ion into the aqueous solution creates a large amount of order. Two of the halide ions stay close to the lanthanide, although beyond the first octahedral water layer, forming the ion pairs $ErCl_2^+$ or ErI_2^+ and giving the over-all compositions $Er(H_2O)_6Cl_2^+$ and $Er(H_2O)_6I_2^+$.

B. CHEMICAL DATA AND THEIR INTERPRETATION

Since, with but few exceptions, the 4f electrons are not actively involved in the chemical reactions of the rare earth metal ions, the main features of the chemistry of these ions are comparable with those of the chemistry of ions in the preceding periodic family. Differences can be explained by the fact that the ionic potential (Z/r , where Z is the ionic charge and r its radius) is larger for the tripositive lanthanide ions than for the alkaline earth metal ions, thus causing stronger electrostatic interaction. Association in solution involves almost exclusively donor halide ions or oxygen. Thus, when the ligand in question is not a chelating agent, the stability of the resulting "complex" is very poor, for the ion-pair attraction is never exceedingly strong.

Association with species containing nitrogen as the sole donor atom rarely, if ever, occurs in aqueous solution, a fact which is well illustrated by the stability constants of complexes formed by tetraethylenepentamine, a chelating agent with five basic nitrogens, with a number of metal ions (466). Although some of the complexes formed were among the most stable obtainable, no measurable interaction was found with lanthanum(III) ion. Compounds with urotropine (110, 115, 133) and methylamine (453) are best described as lattice compounds (405). However, the situation may be different in nonaqueous media. Thus, the compound $Y(\text{dipy})_3 \cdot 3\text{THF}$, where dipy stands for 2,2'-bipyridine and THF for tetrahydrofuran, has been reported (216). It can be recrystallized from tetrahydrofuran solution, and it shows practically zero conductivity in this solvent.

The best known coordination compounds of the lanthanide ions, and perhaps the only ones that really deserve the name, are those involving a chelating agent as the ligand. The situation here is analogous to that existing in alkaline earth metal chemistry, where possible coordinated bonds are not strong enough to cause the metal ion to leave the solvation layer and enter into the complex. Chelating agents increase the free-energy change of this reaction through an entropy effect (413), a common feature of all chelation processes. That this entropy effect is operative with the rare earth metal chelates is substantiated by a number of recent thermodynamic measurements (44, 328, 364, 365, 369, 375, 538), which show that in many cases the entropy contribution of the free-energy change of the process is the determining factor and that the enthalpy term is very small or even opposed to the formation of the complex (section IIIB4).

C. STEREOCHEMICAL CONSIDERATIONS

The existence of polydentate chelates with no symmetry plane suggests the presence of optical isomers. The actual isolation of these isomers depends upon their stability with respect to racemization. First attempts at resolution with the relatively strong ethylenediamine- N,N,N',N' -tetraacetate chelates (372), performed in aqueous solution, failed. However, partial chromatographic resolution of certain acetylacetonate chelates in chloroform and in benzene-petroleum ether solution has been successful (367). Inasmuch as these chelates are thermodynamically less stable than those with ethylenediamine- N,N,N',N' -tetraacetic acid, the successful isolation of optical isomers is no criterion for bond strength or type. Rather, the separation of these isomers is regulated by kinetic effects. These effects are more favorable to racemization in water than in the much less polar chloroform or benzene-petroleum ether.

D. SUMMARY

Bonding in the coordination compounds of yttrium and rare earth metal ions may be considered as involving, fundamentally, electrostatic interaction. Even in the most stable complexes, the bond strength has the same order of magnitude as the free ion-water dipole interaction, since the ΔH values thus far measured for the formation of complexes in aqueous solution are never very large. Thus, it may be predicted that stability would be improved by working in systems where the solvation energy is lower, *e.g.*, in water-dioxane mixtures. As with other cations which have a reduced tendency to form complex species (*e.g.*, the alkaline earth metal ions), the chelate effect overcomes this deficiency. Only polydentate ligands, therefore, can be expected to form stable complexes.

V. APPLICATIONS OF COMPLEX SPECIES

A. FRACTIONAL CRYSTALLIZATION AND PRECIPITATION

Fractional crystallization and precipitation were once the only methods of separating the rare earth metal ions. These relatively tedious methods are based on slight differences in solubilities of isomorphous salts. In a number of cases, the use of coordinating ligands has given better separations than have simple or double salts. Also, precipitation of simple salts in the presence of complexing agents has led to improved separation.

1. Fractionation of Complex Species

Mandelic acid, an α -hydroxylic acid, precipitates the rare earth metal ions, but the solubilities of the mandelates are pH dependent. Thus, these compounds may be continuously fractionated by varying the pH of the solution with ammonia or hydrochloric acid. Unusually large separation factors are reported, probably as a consequence of differences in the stability and solubility of the complexes. The cations studied precipitate in order of increasing ionic radii except for yttrium, which falls between gadolinium and dysprosium (608).

Large differences in solubility among the dimethyl phosphates have been noted (336, 337, 383). The average separation factor, $S = (K_2 + 1)/K_1$, where K_2 is the molar solubility for a given cation and $K_1 + 1$ that for the next cation in the series, is 1.63. This value has been compared with separation factors of 2.5 and 1.9 for the solvent extraction systems HDEHP-HCl and TBP-HNO₃, respectively. The dimethyl phosphates may be chelates similar to the HDEHP compounds containing these cations.

A separation based on the fractional crystallization of $NH_4[LnEDTA]$ has been described. The phase diagrams were studied, and several phases differing in de-

gree of hydration were found. Since different cations tend preferably to crystallize in a certain phase, separations based on these diagrams were devised (68, 70-72). Fractionation using the acids $H[LnEDTA]$ has also been investigated (66).

The hexaantipyrine compounds have been used in separations. Their differentiating ability is thought to be due to the difference in complex stability rather than to large differences in solubility (338).

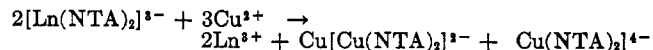
Because quinaldic acid precipitates thorium in the cold whereas lanthanum, cerium, praseodymium, neodymium, yttrium, and mixtures of the yttrium earths are not precipitated, this reagent can be used to remove thorium from these lanthanides.

2. Classical Fractionation in the Presence of Coordinating Agents

If fractionation of simple salts is done in the presence of a complexing agent, the amount of separation is dependent upon two factors, namely the differences in solubility of the simple salts and the difference in the stabilities of the individual complexes. If the complexing agent is an acid derivative, then a factor of pH dependence is introduced also.

The effect of ethylenediamine- N,N,N',N' -tetraacetate on oxalate and sulfate fractionation has been studied (187, 339, 341-343, 592). Results of fractionation of certain pairs of rare earths by homogeneous precipitation of the oxalates through hydrolysis of methyl oxalate, both in the presence and absence of this chelating agent, have been compared. No appreciable difference in separation was found, although the solubilities of the oxalates were reversed for the series (182). With increasing atomic number, the solubilities of the oxalates decrease, and the stabilities of the EDTA complexes increase. The effects of solubility and stability are therefore opposed.

Mixtures of rare earth metal salts have been fractionated by precipitation of the oxalates in the presence of nitrilotriacetic acid by controlling the pH. However, separation factors were not measured, and it is not possible to compare this method with other methods in terms of fractionating efficiency. The species $[La(NTA)_2]^{3-}$ was identified by precipitation of the compound $[Co(NH_3)_6] \cdot La(NTA)_2$ (32). Since nitrilotriacetate forms strong complexes with the elements of the latter part of the series (Table I), the pH must be lowered so much to dissociate the complex that the oxalates now become soluble. This difficulty has been circumvented by use of an exchange reaction with a metal ion which forms complexes with nitrilotriacetic acid that are more stable than the lanthanide complexes. For example, with copper(II) ion the oxalate fractionation can take place at higher pH values, as suggested by the equation



This principle has been used also in ion exchange where an ion such as Cu^{2+} becomes a retaining ion.

B. SOLVENT EXTRACTION

Whereas fractional crystallization is tedious and not easily amenable to adequate repetition of individual operations, solvent extraction can be operated continuously and can, in terms of a countercurrent arrangement, amount to an almost infinite number of separational steps. As is characteristic of all techniques of separation, no known reagent can give clear-cut separations between adjacent lanthanides, unless, as is true in only a limited number of cases, these elements can exist in two different oxidation states. Solvent extraction is also desirable in that it is applicable to conditions of large ion concentration. Fractional crystallization and ion exchange, by contrast, are limited in the quantities of materials that can be used by solubility and exchanger capacity, respectively.

1. Extraction with Tri-*n*-butyl Phosphate (TBP)

The esters of various phosphorus-containing acids are the most widely investigated of the extracting agents. Tri-*n*-butyl phosphate (TBP) has been used as an extractant both as such and when diluted with various organic solvents. The extractability of the lanthanides from moderate to large concentrations of hydrochloric acid or nitric acid increases with increasing atomic number. However, with small concentrations of nitric acid (0.3 *M*), the order is reversed (420). Yttrium falls near holmium in its proper place on the usual basicity scale (370a). The extractability (420) of scandium exceeds that of all the rare earth metal ions. As a consequence, this element may be easily purified by this method.

Extractability of the tripositive ions increases with increasing nitric acid concentration, but it is also large at low acidity and high nitrate ion concentration (483). There is a region of decreasing distribution coefficients at about 4-7 *M* HNO_3 (483). The extracted species appear to be $Ln(NO_3)_3 \cdot 3TBP$, where Ln is Ce, Tb, Tm, and Y (210). The species $[Ln(TBP)_a(H_2O)_{x+a}](NO_3)_3$, where $x = 6$, has been postulated but x may be dependent on atomic number, being larger at lower atomic numbers (419). This formulation has been disputed (217).

Separation factors (ratio of distribution coefficients of adjacent lanthanides) are about two at high nitric acid concentration (483). When the distribution coefficient is plotted against atomic number for the entire series, one group of authors found that two straight lines crossing at element 64 fit the data (419). By contrast, other workers found an "odd-even effect," when

careful attention was given to controlling the experimental variables (217). However, this effect was not noted by still other investigators (356).

Another nitrate-tributyl phosphate system with an $\text{LiNO}_3\text{-KNO}_3$ eutectic melt as one phase has been described (247). Distribution coefficients are $10^2\text{-}10^3$ higher for this system than for the concentrated aqueous nitrate system. The extracted species, $\text{Ln}(\text{NO}_3)_3 \cdot 3\text{TBP}$, is thought to be the same as has been reported for the aqueous system. Addition of chloride to the nitrate melt lowers the distribution coefficient, but in some cases the separation factor is increased. For comparison, the factor for $\text{Eu}^{3+}\text{-Nd}^{3+}$ is 3.8 for the pure melt and 4.5 when chloride has been added. An average separation factor for TBP- HNO_3 system is 1.9 (428).

Systems with other anions have been studied also. In the TBP- HClO_4 system, cerium(III) and promethium ions have the same partition coefficient over the total range of acidities studied (507). This means that the separation factor is unity and that no separation can result. Since it is well known that the perchlorate ion is a poorer coordinating agent than nitrate ion, it is evident by comparison of the two systems that the anion must play an important role in coordination. Distribution ratios for the system $\text{Ln}^{3+}\text{-NH}_4\text{SCN-TBP}$ have been determined and compared with an ion-exchange sequence where thiocyanate ion was used as an eluting agent (644). The distribution ratio decreases with increasing acidity because of extraction of thiocyanate ion with acid into the organic phase. The composition of the extracted europium(III) complex, for example, was probably $\text{Eu}(\text{SCN})_3(\text{TBP})_4$ under the conditions studied.

Since separation appears to depend, at least to a certain extent, on complex formation in the aqueous phase, it is reasonable to assume that addition of complexing agents to the aqueous phase, or, for that matter, to the organic phase, could enhance separation. This possibility has been investigated with varying results. Lactic acid in the aqueous phase decreases the extractability and gives poorer separation when TBP is used as an extraction agent (483). If ethylenediamine- N,N,N',N' -tetraacetate is used, however, there is an increase in separation for the yttrium-group cations but not for those of the cerium group (356). In the series holmium to ytterbium, the separation factor increases 2.5-3 times. For a neighboring pair of elements it reaches 3-3.5. These results have been explained in terms of equilibrium principles (356).

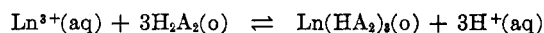
Addition of chelating agents to the organic phase gives somewhat unexpected results. The extractability is raised as might be expected, although separation factors are not improved. Later studies demonstrated a synergistic effect (208, 209). When the rare earths are extracted with thenoyltrifluoroacetone

(TTA) in the presence of TBP, a large enhancement of the distribution coefficient was noted, an enhancement that was larger than the sum of the distribution coefficients of either extracting agent taken separately. This change was thought to be due to the formation of a species $\text{M}(\text{TTA})_3(\text{TBP})_2$ which would be quite easily extracted into the organic phase. Phosphorus extracting agents other than tributyl phosphate also give this effect.

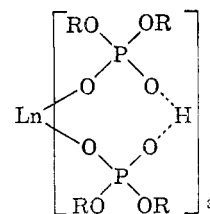
2. Extraction with Acidic Phosphate Esters

The monoalkyl and dialkyl phosphates have been studied by many workers (119, 120, 300, 423, 425, 428, 429, 440, 499, 607). The extracting agents studied include dibutyl phosphate (119, 120, 300, 607), bis(2-ethylhexyl)phosphoric acid (425, 428, 429, 440), bis(amyl)phosphoric acid (415), bis[*p*-(1,1,3,3-tetramethyl)phenyl]phosphoric acid (425), mono(2-ethylhexyl)phosphoric acid (425), mono[*p*-(1,1,3,3-tetramethyl)phenyl]phosphoric acid (425), and various mono-*n*-alkylphosphoric acids.

The extraction of lanthanides with dialkylphosphoric acids shows an inverse third-order dependence on hydrogen ion concentration and a direct third-order dependence on the concentration of the extracting agent. Inasmuch as the dialkylphosphoric acids have been shown to be dimeric in the organic phase, the extraction process may be represented by the equation (119)



There are conflicting data concerning the correct equation. Some investigators suggest a second-order dependence on hydrogen ion concentration and extracting-agent concentration (499). Added salts have no effect on the extraction. No anions appear in the organic phase. If ytterbium(III) is extracted with an equimolar quantity of dibutylphosphoric acid (HDBP) in carbon tetrachloride, an unsolvated compound, $\text{Yb}[\text{DBP}]_3$, is obtained (300). From a study of the solubility of this compound in carbon tetrachloride with the ester present in different amounts, it was concluded that the compound $\text{Yb}[\text{H}(\text{DBP})_2]_3$ formed. The solvation equilibration constant was estimated at 0.1. The structural formula proposed for the extracted species is (425)



For bis(2-ethylhexyl)phosphoric acid (HDEHP), a plot of the distribution coefficient *vs.* atomic number gives a straight line, with the yttrium ion falling at the

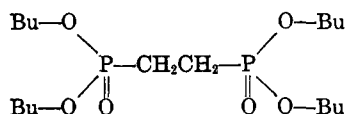
hypothetical atomic number 67.6. The average separation factor is 2.5 (428). However, dibutylphosphoric acid gives two straight lines meeting at gadolinium, with separation factors of 1.95 and 2.6 for light and heavy earths, respectively (119, 120).

The effects of molecular size of the extraction agent on the extraction of certain lanthanide ions have been studied using hydrogen 2-ethylhexyl phenacyl phosphonate. Although several resulting chelate structures were proposed, the stoichiometry of the reactions studied must not be regarded as having been definitely determined (606). By contrast with other organophosphorus reagents, ethylhexyl phenacyl phosphonate does not efficiently separate lanthanum from yttrium (606).

The compound hydrogen 2-ethylhexyl phenyl phosphonate behaves like the dialkyl phosphates in extraction of the rare earth metal ions. It gives better separation factors than bis(2-ethylhexyl)phosphoric acid (2.8 vs. 2.5) (426).

Extraction with monoalkylphosphoric acids has been investigated, but the mechanism of extraction is not well understood. Both a chelate and a "polymer" extraction mechanism have been proposed (425, 607).

Both phosphonic and phosphoric esters have been used for the extraction of europium after reduction to the divalent state. Separation factors, as might be expected, are quite large for the pairs Pm(III)-Eu(II), Sm(III)-Eu(II), and Gd(III)-Eu(II) (423). Yet another type of phosphorus compound, tetrabutyl ethylenediphosphonate



has been investigated. Although this compound closely resembles tributyl phosphate, it could have a chelating effect. The distribution coefficients for yttrium and the lanthanide ions decrease very rapidly with increasing nitric acid concentration (475).

3. Extraction with 1,3-Diketones

Solvent extraction of rare earth metal ions into acetylacetone increases with decreasing acidity. Separation of the lanthanides also increases with decreasing acidity. The solubility of rare earth metal acetylacetonates in acetylacetone increases with atomic number, and a straight line results when the logarithm of solubility is plotted against ionic radius. However, the per cent of extraction does not vary regularly (64). Counter-current extraction of the acetylacetonates using various organic solvents is complicated by hydrolysis. In order to prevent this, excess acetylacetone is added to the system, but this decreases extraction. Adding methanol helps to increase extraction (63, 603), but not the separation factor.

Various specialized separations have been carried out using 1,3-diketones as extracting agents. Acetylacetone and thenoyltrifluoroacetone extract cerium from various radioactive elements (511, 557, 558). Thenoyltrifluoroacetone has been used to separate yttrium-strontium-90 mixtures (556). Benzoylacetone separates lanthanum-140 from barium-140 (536).

4. Extraction with Miscellaneous Agents

Extractions of scandium and rare earth metal ions with 8-quinolinol, halogen-substituted 8-quinolinols, and cupferron have been studied (121, 126, 370, 582). As yet there are insufficient data to permit evaluation of separational efficiency. Other extracting agents, which have been only partially studied, are picrolonic acid (389), salicylic acid (553), and the β -isopropyl derivative of tropolene (123). Cerium can be removed from many mixtures by oxidation to the quadrivalent state and subsequent extraction from nitric acid as the free acid $\text{H}_2[\text{Ce}(\text{NO}_3)_6]$ or some salt thereof (53, 54, 294, 345, 495).

5. Reverse-Phase Partition Chromatography

In reverse-phase partition chromatography, a liquid extraction agent or a chelating agent is suspended on an inert support. The rare earth metal ions to be separated are placed on the top of the column and eluted with either concentrated acid or an acidic solution of the extracting agent. This method would appear to combine the high separation factors of solvent extracting agents and the attractiveness of concentrated rare earth solutions with the repetitive nature and simplicity of a column technique.

Earlier the use of 8-quinolinol suspended on a support of cellulose and eluted with an oxine solution was investigated qualitatively (448, 449). More recently bis(2-ethylhexyl)phosphoric acid (80, 438, 439) and tributyl phosphate (145, 508) have been shown to give rather good separations on the tracer level. The separation of samarium, neodymium, praseodymium, and lutetium on a tributyl phosphate column has been attempted on a macro scale (349). Although there was overlap among the eluted bands, the investigators felt that with better conditions separations could be improved. The concentrations of the eluted fractions were up to 20 g. of oxide per liter.

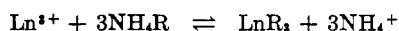
C. ION EXCHANGE

1. Cation Exchange

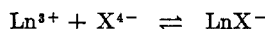
a. Simple Theory

Perhaps the most widely investigated of the newer methods for separating the rare earths is the elution, with a complexing agent which is usually a chelating

agent, of the tripositive ions adsorbed on a cation-exchange resin. The competing equilibria are, for an ammonium-cycle resin (R)



and, for a tetranegative chelating ion (X^{4-})



The first equation is described by a distribution coefficient (λ_0)

$$\lambda_0 = [\text{Ln}_r^{3+}]/[\text{Ln}_s^{3+}] \quad (\text{Eq. 1})$$

where the total concentrations in resin (r) and solution (s) are included, and the second by a formation constant (Tables II and III)

$$K_{\text{Ln}} = [\text{LnX}^-]/[\text{Ln}^{3+}][\text{X}^-] \quad (\text{Eq. 2})$$

It can be shown (352, 361, 456, 578) that for adjacent tripositive ions (Ln^{3+} and Ln'^{3+}), a separation factor (α) can be expressed as

$$\alpha = \lambda_0' L_{\text{Ln}} / \lambda_0 K_{\text{Ln}}' \quad (\text{Eq. 3})$$

Inasmuch as λ_0 and λ_0' differ from each other only very slightly, the degree of separation that can be obtained is determined by the difference between the two formation constants. These considerations apply when but a single neutral or anionic complex species is formed in reaction of the chelating agent with the cation. If cationic complexes are formed or more than a single species is present, the separation factor cannot be so simply defined. The citrate systems, for example, are described in more complicated terms (528).

In principle, treatment of a resin, at the top of which a mixture of rare earth metal ions has been adsorbed, with an appropriate chelating agent should remove these cations in the order of the stabilities of the resulting chelates. If the resin ahead of the band of adsorbed ions contains a cation (*e.g.*, NH_4^+) that is much less strongly complexed than the lanthanide ions, all cations tend to spread throughout the column, and little separation occurs as a consequence of overlapping of the elution bands. If, however, the resin contains a cation that is more strongly complexed than the lanthanide ions, that cation will permit resorption of the lanthanide ions on the exchanger only when the equilibrium concentration of the chelating ion is adequate and thus serve as a retaining ion to prevent diffusion of the elution bands. The sharpened band fronts that result permit infinite equilibration of each lanthanide ion between solution and resin phases and thus take full advantage of differences in chelate stability in terms of Eq. 3.

b. Hydroxycarboxylic Acids

The two common types of chelating agents studied as eluting agents for ion-exchange separation are the hydroxycarboxylic acids and the aminopolycarboxylic acids.

Citric acid has been investigated extensively (218, 273, 523–525, 528). The complex species at low pH is apparently $[\text{Ln}(\text{H}_2\text{cit})_3]$ (575), whereas at higher pH the species is $[\text{Ln}(\text{cit})_2]^{3-}$ (527, 528). The order of elution of the rare earth metal ions with a citrate buffer of pH 3.28 is Lu^{3+} to Sm^{3+} in the inverse order of atomic numbers (273).

α -Hydroxyisobutyric (87, 351, 512), glycolic (547), and lactic (157, 626) acids have also been investigated. The separation factors for α -hydroxyisobutyric acid are comparable to those of ethylenediamine-N,N,N',N'-tetraacetate, and this eluting agent may be superior to the latter as a consequence of better flow rates and solubility characteristics (87).

Lactic acid is more selective than citric acid, giving virtually complete separation on a tracer scale when gradient elution with a lactic acid solution at 87° and pH 3 is used (157). The order of elution of the ions studied was Y^{3+} , Tb^{3+} , Gd^{3+} , Eu^{3+} , Sm^{3+} , Pm^{3+} , and Nd^{3+} . A quantitative comparison of the elution of the rare earth metal ions with that of certain of the actinide ions has been made with lactic acid as the complexing agent (626).

The separational efficiencies of the α -monohydroxycarboxylic acids of different chain lengths have been compared. There is an optimum chain length for maximum selectivity; *e.g.*, the heavier cations are better separated with ammonium lactate and the lighter elements with ammonium α -hydroxyisobutyrate. Glycolic acid separates dysprosium from yttrium (457).

c. Aminopolycarboxylic Acids

The formation constants of the chelates of adjacent rare earth metal ions with various aminopolycarboxylic acids are sufficiently different to make these reagents useful for ion-exchange separations (Eq. 3). As already pointed out (section IIIB3), $\log K$ increases roughly regularly with atomic number for the chelates of certain of these acids (*e.g.*, ethylenediamine-N,N,N',N'-tetraacetic and 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic), making species of this type potentially useful for separations involving the entire lanthanide series. Irregularities among the formation constants of chelates characteristic of others of these acids could cause some elements to elute together but could also position yttrium with the cerium earths, from which it can be separated rather readily. The two tetraacetic acids mentioned above are insoluble as such and precipitate if the acidity of the system is too high.

Elution of a column on the ammonium cycle with a solution of ethylenediamine-N,N,N',N'-tetraacetate adjusted to a pH of 3.5 gives some separation (322). In another method, a calculated amount of this chelating agent was added to a mixture of rare earths to complex partially the rare earth metal ions present. When

this solution was passed through an ion-exchange column, the less readily complexed ions remained on the column, whereas the more readily complexed cations passed through (621), thus giving a crude fractionation for the preparation of concentrates for subsequent detailed separation. In the presence of retaining ions—originally iron(III) but much more effectively copper(II) (69, 324, 530, 531)—however, separation of the various tripositive species on essentially any scale and in remarkably high states of purity has been achieved. Under appropriate conditions of pH, sharp band fronts are readily maintained, and copper(II) ion leads all but the heaviest lanthanide ions down the column. Precipitation of the copper compound $\text{Cu}[\text{Cu}(\text{EDTA})]$ may occur over a period of time (344), but it is not normally a problem (69, 344). The use of this general procedure and a somewhat comparable one involving N' (2-hydroxyethyl)ethylenediamine- N,N,N' -triacetic acid for separations on a large scale is important (456).

Nitrilotriacetic acid has also been used as an eluent (150, 232, 323, 352, 609, 632). Inasmuch as this complexing anion has four donor sites and a -3 charge, several chelated species are possible. In deriving an equilibrium theory for separation, one author considered only a neutral species, $\text{Ln}(\text{NTA})$, as the complex present (352). Another has shown that the species $\text{Ln}(\text{NTA})_2^{3-}$ can be prepared by precipitation of this anion as the compound $[\text{Co}(\text{NH}_3)_6][\text{Ln}(\text{NTA})_2]$ (32). Formation constant data for both $\text{Ln}(\text{NTA})$ and $\text{Ln}(\text{NTA})_2^{3-}$ are available (8, 365). From a polarographic study of the system Eu^{3+} -NTA, the complex formed was found to be $[\text{Eu}_2(\text{NTA})_3]^{3-}$ (394). This finding has been questioned (8). The equilibria between the rare earths and the sodium, copper, and nickel forms of a cation-exchange resin have been studied also (394). From the constants so determined, the effectiveness of separation of adjacent rare earth metal ions was calculated. The position of yttrium ion in elution series depends both on the stability of its chelate and on its ion-exchange affinity. The stability constant falls between those for the ions Sm^{3+} and Eu^{3+} , and its ion-exchange affinity between those of the ions Dy^{3+} and Ho^{3+} . In the elution series, yttrium was calculated to fall between the Gd^{3+} and Tb^{3+} ions (394).

The acid N -(2-hydroxyethyl)iminodiacetic acid also has been studied as an eluent (628-631). Both cationic and anionic complexes appear to play a role in the separation (630).

d. Miscellaneous Eluting Agents, Separations, and Methods

The triphosphate ion forms anionic complexes with the tripositive lanthanide ions and may be used as an eluting agent with both cationic and anionic exchangers (551, 552).

Thenoyltrifluoroacetone will separate the rare earth metal ions on cation exchangers when water-dioxane is used as the solution phase (259). Complete separation of yttrium from europium on a tracer scale was obtained on very short columns. The successful use of water-insoluble thenoyltrifluoroacetone suggests the use of the water-dioxane solvent system for other water-insoluble complexing agents (259).

The species present in ion-exchange separations using thiocyanate as a ligand are thought to be $\text{Ln}(\text{SCN})_2\text{Cl}$. A separation factor for adjacent rare earths of about 1.1 to 1.2 was obtained (201). This is somewhat smaller than that reported for α -hydroxyisobutyric acid (1.6) (201, 512).

A novel method, which uses the technique of electromigration on ion-exchange membranes in the presence of ethylenediamine- N,N,N',N' -tetraacetate, has been described. Separation is dependent on the difference in stability of the complexes of the metal ions to be separated (60).

Ion exchange has been used for the preparation of pure yttrium (12, 325) and pure scandium (200, 529). The polyaminepolycarboxylate DTPA was used with an exchanger on the hydrogen cycle. This works well, because yttrium then falls between neodymium and samarium, instead of in its usual place between terbium and dysprosium. Two agents which elute its cation in different places will give pure yttrium (12). Copper(II) and lead(II) ions have been used as retaining ions in the purification of scandium because they retain rare earth metal ions but allow the passage of the scandium ion (529).

Other applications include the separation of lanthanum from barium (301) and of the actinides from the lanthanides (130).

e. Comparison Studies

The relative efficiencies of separation for a number of complexing agents, including ethylenediamine- N,N,N',N' -tetraacetic, nitrilotriacetic, glycolic, malic, citric, tartaric, and acetic acids, have been determined (353, 594). Some aminopolycarboxylic acids have also been compared. Thus, the order of increasing efficiency of separation is ethylenediamine- N,N,N',N' -tetraacetate, 1,2-diaminocyclohexane- N,N,N',N' -tetraacetate, 2,2'-bis[di(carboxymethyl)amino]diethyl ether, and 1,2-bis[2-di(carboxymethyl)aminoethoxy]ethane (231).

Elution orders of many cations including the rare earths have been determined for the EDTA and HEDTA systems (260). The theory for the separation of a dipositive ion from a tripositive ion has been derived and tested for Tm^{3+} and Zn^{2+} . The separation factor depends on both the composition of the mixture and the pH (260).

2. Anion Exchange

A separation by anion exchange, using a given chelating agent, depends on somewhat different factors from one by cation exchange, using the same chelating agent (604). For example, when the complexing agent is ethylenediamine-N,N,N',N'-tetraacetate, the order of elution is not the inverse order of stability constants as it is in cation exchange. Rather, it is Lu^{3+} , Yb^{3+} , Tm^{3+} , Er^{3+} , Ho^{3+} , La^{3+} , Dy^{3+} , Ce^{3+} , Tb^{3+} , Pr^{3+} , Nd^{3+} , Gd^{3+} , Pm^{3+} , Sm^{3+} , and Eu^{3+} (357). The distribution coefficient increases from La^{3+} to Eu^{3+} and then decreases with increasing atomic number. This decrease in distribution coefficient appears to be due to a steric effect in the complex anion, which involves the degree of hydration (604). Infrared spectra of compounds of the type $\text{H}[\text{Ln}(\text{EDTA})]$, in the region of carboxyl stretching, lend some support to the concept of different anion structures for different rare earth metal ions (604). The separation factors for pairs of neighboring cations are 2.92, 1.49, 1.34, 1.27, 1.15, and 1.11 from La^{3+} to Eu^{3+} and 0.66, 0.53, 0.45, 0.51, 0.54, 0.64, 0.63, and 0.76 from Eu^{3+} to Lu^{3+} (358).

Citrate has also been used as an eluting agent for anion exchange. The order of elution is the reverse of the order for cation-exchange resins (243, 288).

Distribution coefficients between an anion-exchange resin and the ions Y^{3+} , Nd^{3+} , Pr^{3+} , and La^{3+} were measured, using sulfuric acid-water-ethanol as the solution phase (131, 476). For La^{3+} the coefficient (γ_0) varied from 1000 to 100 as the acid concentration was increased from 0.001 to 0.1 *N*. The distribution coefficient for a given cation decreased with increasing ammonium sulfate concentration and increased with increasing ethanol concentration. At constant sulfuric acid and ethanol concentrations, the adsorbability increased in the order $\text{Nd}^{3+} < \text{Pr}^{3+} < \text{Y}^{3+} < \text{La}^{3+}$. With the exception of yttrium ion, this is the order of increasing crystal radii. This method offers little use as a separational technique because of low separation factors and low solubility of rare earth metal sulfates in this medium.

Anion-exchange separation in nitric acid-ethanol medium has been investigated (130). Distribution ratios so increase with increasing ethanol concentration that elution with water must be used in order to remove lanthanum and neodymium from the column (130). Separation also increased with increasing ethanol concentration. The separation of thorium from the rare earths by anion exchange in 5 *M* nitric acid solution has been described, with praseodymium being used as a representative rare earth (100). The distribution coefficient for praseodymium ion as a function of nitric acid concentration is a maximum at about 7 *M* nitric acid and decreases rapidly at higher acid concentrations.

Using 3–4 *M* lithium nitrate solutions as the solution phase, separation factors of *ca.* 1.4 for adjacent cations have been found for the series from La^{3+} to Eu^{3+} . These compare favorably with 1.6 for α -hydroxyisobutyric acid or ethylenediaminetetraacetate with a cation exchanger (334). Gradient elution provides separation on the tracer scale in the order Cs^+ , Ba^{2+} , Yb^{3+} , Eu^{3+} , Sm^{3+} , Nd^{3+} , Pr^{3+} , Ce^{3+} , and La^{3+} . Separation factors are much lower for the elements beyond europium.

Apparently in lithium nitrate solutions, the distribution coefficient continues to increase (334) with concentration, by contrast with what is observed with nitric acid solutions (100).

It has been found also that actinium is removed before lanthanum when an anion-exchange column is eluted with lithium nitrate solution. This order is in contrast to that on the basis of crystal radii (La^{3+} , 1.06 Å.; Ac^{3+} , 1.11 Å.). The adsorbability of actinium lies between those of samarium and neodymium. That actinium also concentrates between samarium and neodymium in the fractionation of the magnesium double nitrates has suggested that elution order could be correlated with the solubilities of the double nitrates (101). The solubility of these salts increases in the order $\text{La}^{3+} < \text{Ce}^{3+} < \text{Pr}^{3+} < \text{Nd}^{3+} < \text{Sm}^{3+}$, which is the reverse of the adsorbabilities. Crystalline double nitrates of the heavy earths do not form, which is also in accord with their weak adsorption on anion-exchange resins (101).

An anion-exchange study of the thiocyanate complexes of the lanthanide ions shows no trend of elution similar to that in cation-exchange elution with thiocyanate (554). From a theory developed, it appears that the cations should elute in the order of atomic number if complexes with the same charge are formed. Covalent bonding is suggested as an explanation for the observation that they do not elute in this order (554). Better explanations, perhaps in terms of steric effects (604), may exist.

It is known that rare earth metal ions are adsorbed on anion-exchange resins from sulfite solutions (597), but no separational studies have been made.

Amine extraction of nitric acid solutions of rare earth metal ions has been investigated and found to be mechanistically more similar to anion exchange than to tributyl phosphate extraction (245). Amine extraction has been applied to the separation of the actinides from the lanthanides (378). Cerium(IV) has also been extracted with trioctylamine. The ion $\text{Ce}(\text{NO}_3)_6^{2-}$ appears to be the extracted species (7).

D. ANALYTICAL APPLICATIONS

Chelatometric titrations have been widely used to determine the rare earth metal ions, either individually or as a group. Ethylenediamine-N,N,N',N'-tetraacetate,

in particular, has been widely used. A review with many references to the application of this reagent to the analysis of rare earths has been published (152). Even microquantities of rare earths have been determined with 0.001 *M* reagent (82).

In order to determine the rare earth metal ions individually, one of the procedures reviewed above must normally be used for prior separations. For example, a determination of rare earth metals obtained as fission products has been described using an ion-exchange method for separation and titration with the reagent EDTA to determine the chemical yield (150).

Color reagents have been developed for the spectrophotometric determination of these cations. Certain of these reagents give very sensitive color reactions, but unfortunately many other cations, anions, and chelating agents interfere. The main problem is to separate the rare earth metal ions from impurities before determination. Some of the reagents used recently for the determination of rare earths are arsenazo, 3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid (166, 401, 402); PAN, 2-pyridylazo-2-naphthol (501); and Xylenol Orange, 3,3'-bis[N,N-di(carboxymethyl)aminomethyl]-*o*-cresol sulfonophthalein (577). Tiron, disodium 1,2-dihydroxybenzene-3,5-disulfonate (202); PAR, 4-(2-pyridylazo)resorcinol (516); and α -(2,4-dihydroxyphenylazo)pyridine (75) are the more sensitive reagents for scandium. However, a large number of ions interfere with these reagents. Tetra-valent cerium has been determined colorimetrically with 8-quinolinol N-oxide (45).

VI. RELATIONSHIP TO SCANDIUM CHEMISTRY

A. INTRODUCTION

Scandium, like its congeners yttrium and lanthanum, appears only in the +3 oxidation state in its compounds. Although it is probably not completely correct to extend the previously developed concepts of ionic interaction between ligand and cation to tripositive scandium, it is still reasonable to assume that for a given complex species, thermodynamic stability will increase in the series La^{3+} - Y^{3+} - Sc^{3+} , paralleling a decrease in crystal radius (La^{3+} , 1.06 Å.; Y^{3+} , 0.88 Å.; Sc^{3+} , 0.68 Å.) (650). This order reflects an increase in cationic charge density, which determines the strength of the ligand-cation bond. Change in charge density is also reflected in change in electronegativity x (La , 1.08; Y , 1.11; Sc , 1.20), as calculated from the relationship (5)

$$x = \frac{0.359Z_{\text{eff}}}{r^2} + 0.744 \quad (\text{Eq. 4})$$

Experimental data (section VIB1) agree with these assumptions.

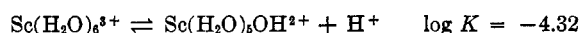
Although the chemistry of scandium is quite generally parallel to that of the rare earth elements (583),

there are also noteworthy similarities to the chemistries of aluminum, vanadium, chromium, and iron (281, 458, 542, 583), and scandium has not been geochemically concentrated to any great extent with the rare earth elements (56). Available reviews describing physico-chemical properties (479), analytical methods (39), and other characteristics (473) can be consulted for detailed comparisons.

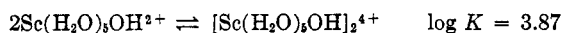
B. SCANDIUM-CONTAINING COMPLEX SPECIES

1. Some Comparisons with Those of the Rare Earth Metal Ions

The scandium(III) ion is more extensively hydrolyzed than the lanthanide(III) ions. At pH > 2.5 and 25°, the equilibria



and



have been described (275). Further hydrolysis leads to the formation of a series of polynuclear "core and link" complex species, of which $\text{Sc}[(\text{HO})_2\text{Sc}]_n^{(3+n)+}$ ($n = 1, 2$) are typical. The species $[\text{Sc}_2(\text{OH})_2]^{4+}$ and $[\text{Sc}_3(\text{OH})_4]^{5+}$ are probably present as well (46). Similar reactions are characteristic of many metal ions (509). Scandium acetate is 9.36% hydrolyzed in 0.414 *N* solution and 17.14% hydrolyzed in 0.02 *N* solution, whereas yttrium and lanthanum acetates are, respectively, 0.71 and 0.31% hydrolyzed in 0.1 *N* solution (542). The same trend is apparent in the free energies of hydration (all in kcal./mole) of the various tripositive ions: Sc^{3+} , -1036; Y^{3+} , -956; La^{3+} , -978; Ce^{3+} , -940 (311).

The compound $\text{Sc}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ can be precipitated selectively at pH 4.9 in the presence of a pyridine-pyridinium ion buffer (348, 404), in keeping with the decreased basicity of the Sc^{3+} ion (370a). Scandium hydroxide 3-hydrate is readily obtained by adding water to scandium trichloroacetate (467), whereas the analogous reactions with yttrium and the rare earth metal compounds give the carbonates (467). Scandium hydroxide is precipitated by alkalis such as aqueous ammonia (148), but these reactions are not selective. The isolation of the compound $\text{Na}_3[\text{Sc}(\text{OH})_6] \cdot 2\text{H}_2\text{O}$ from concentrated aqueous sodium hydroxide solutions (248, 251) indicates amphoteric behavior (542). Yttrium and the rare earth metal hydroxides are much less acidic (370a). Disagreements as to the composition and structure of scandium hydroxide (484, 610, 611) are not pertinent to this discussion. For comparison, the standard free energies of formation of $\text{Sc}(\text{OH})_3$ and $\text{Lu}(\text{OH})_3$ are, respectively, -294.66 and -152.62 kcal./mole (651). The solubility product constant of $\text{Sc}(\text{OH})_3$, 2×10^{-30} g.-ion⁴ l.⁻⁴ at 25° (2), is smaller than those for $\text{Ln}(\text{OH})_3$ (370a).

Halodihydroxo complexes are formed in aqueous scan-

TABLE V
 CONCENTRATION-QUOTIENT FORMATION-CONSTANT DATA AT 25°

Equation	Concentration-quotient data			
	F (416)	F (307)	Cl (416)	Br (416)
$\text{Sc}^{3+} + \text{X}^- \rightleftharpoons \text{ScX}^{2+}$	1.55×10^6	1.2×10^7	11.7	16.1
$\text{ScX}^{2+} + \text{X}^- \rightleftharpoons \text{ScX}_2^+$	1.89×10^6	6.4×10^5	10.9	3.3
$\text{ScX}_2^+ + \text{X}^- \rightleftharpoons \text{ScX}_3$	1.19×10^4	3.0×10^4
$\text{ScX}_3 + \text{X}^- \rightleftharpoons \text{ScX}_4^-$...	7.0×10^2
$\text{Y}^{3+} + \text{X}^- \rightleftharpoons \text{YX}^{2+}$	8.5×10^3	...	2.3	2.8
$\text{YX}^{2+} + \text{X}^- \rightleftharpoons \text{YX}_2^+$	1.6×10^3
$\text{YX}_2^+ + \text{X}^- \rightleftharpoons \text{YX}_3$	1.6×10^3

dium halide solutions (2, 250). The hydrolysis product $\text{Sc}(\text{OH})\text{SO}_4$ has been obtained from sulfate solutions (250). When scandium oxide is added to boiling solutions of HX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), compounds of the type $\text{Sc}(\text{OH})\text{X}_2 \cdot 5\text{H}_2\text{O}$ are obtained (435). The analogous $\text{Sc}(\text{OH})(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ has been described (478). The solubility product constant of $\text{Sc}(\text{OH})_2\text{Cl}$ is 2.19×10^{-22} g.-ion⁴ l.⁻⁴ at 25° (2). Comparable hydroxo species of the rare earth metal ions are less well characterized.

Formation-constant data for the species MX^{2+} , MX_2^+ , and MX_3 , as summarized in Table V, show the scandium complexes to be more stable than their yttrium analogs (307, 416). Other data for MCl^{2+} complexes, based upon solubility differences between 0.5 *M* HCl and 0.5 *M* HClO₄ solutions at 25°, are: ScCl^{2+} , 1.75; LaCl^{2+} , 2.9; SmCl^{2+} , 2.9; YbCl^{2+} , 3.6; LnCl^{2+} , 3.0 g.-ion l.⁻¹ (514). These values have been less accurately determined than those given in Table V. The enthalpy data (55) given in Table VI suggest that hydration number increases in the series Sc^{3+} - Y^{3+} - La^{3+} and then decreases in the series La^{3+} - Lu^{3+} but give no definitive idea on stability trends of chloro complexes. Differences between adjacent rare earth metal ions are small (55, 321).

The composition $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ has been observed in a phase diagram of the CsCl - ScCl_3 system (197). However, the thiocyanate ion (a pseudo-halide), on the basis of a spectral study using an LiCl - KCl eutectic (206), showed no evidence of forming complex species with scandium ion. On the other hand, scandium ion is preferentially extracted from aqueous thiocyanate solutions by diethyl ether (52, 146, 147), suggesting some interaction with thiocyanate ion. Furthermore, compounds of the type $\text{M}^I_3\text{Sc}(\text{SCN})_6 \cdot 4\text{H}_2\text{O}$ ($\text{M}^I = \text{NH}_4, \text{K}$) have been isolated from aqueous solution (47) and reported to be similar to their vanadium and chromium analogs (583). Anion-exchange studies also indicate the presence of a thiocyanatoscandium(III) complex (580). Several equilibria involving chloride and thiocyanate ions have been described (200).

The fluoro complexes of scandium are particularly stable. Although the compounds $(\text{NH}_4)_2[\text{ScF}_6]$ and $\text{NH}_4[\text{ScF}_4]$ have been described (540), those containing the species $[\text{ScF}_6]^{3-}$ are more common. Scandium can

 TABLE VI
 ENTHALPY DATA FOR M^{3+} AND MCl_3

Chloride	X-Ray diffraction type	$-\Delta H_{\text{form}}$	$-\Delta H_{\text{soln}}$	$-\Delta H_{\text{form}}$
		(of $\text{M}(\text{aq})^{3+}$), kcal./mole	(of MCl_3), kcal./mole	(of MCl_3), kcal./mole
ScCl_3	β or γ	149.8	47.1	220.7
YCl_3	γ	168.3	52.3	234.8
LaCl_3	α	176.5	31.6	263.7
GdCl_3	α	168.8	42.4	245.2
LuCl_3	γ	160.3	51.3	227.8

be precipitated quantitatively as the salt $[\text{Co}(\text{NH}_3)_6][\text{ScF}_6]$ (541) and removed from the rare earths by adding excess fluoride ion, which gives precipitates of LnF_3 with the latter (384). The crystal structure of scandium fluoride suggests the existence of ScF_6^{3-} groups (395, 396), whereas those of yttrium and the rare earth metal fluorides do not (386).

Scandium chloride is much more soluble in alcohols than are yttrium and the tripositive rare earth metal chlorides (149). In such solutions, six molecules of the alcohol ($\text{C}_n\text{H}_{2n+1}\text{OH}$, $n = 1-9$) apparently associate with each molecule of ScCl_3 (278), but the solid alcoholates isolated from such solutions contain less alcohol. A variety of alcoholates $\text{ScCl}_3 \cdot n\text{ROH}$ have been obtained by reaction of anhydrous scandium chloride with alcohol vapors (432).

Under anhydrous conditions, ammonia gives the compounds $\text{ScX}_3 \cdot n\text{NH}_3$ ($n = 2, 4, 5$; $\text{X} = \text{Cl}, \text{Br}$), but in the presence of water, hydroxoscandates, containing no $\text{Sc}-\text{NH}_3$ bonds, result (274). Anhydrous scandium chloride forms adducts $\text{ScCl}_3 \cdot 3\text{NH}_2\text{R}$ and $\text{ScCl}_3 \cdot 3\text{NHR}_2$ with a number of alkyl primary and secondary amines and $\text{ScCl}_3 \cdot \text{NR}_3$ with at least triethyl- and tri-*n*-octylamines (279). The adducts $\text{ScCl}_3 \cdot 3\text{C}_2\text{H}_4(\text{NH}_2)_2$, $\text{ScX}_3 \cdot 4\text{NH}(\text{C}_2\text{H}_5)_2$, $\text{ScX}_3 \cdot \text{NH}(\text{i-C}_3\text{H}_7)_2$, and $\text{ScBr}_3 \cdot \text{N}(\text{C}_2\text{H}_5)_3$ ($\text{X} = \text{Cl}, \text{Br}$) have been reported as reaction products in anhydrous ethanol (561). Ammonolysis to give amides occurs in the presence of water with the primary and secondary amine adducts (145), but the tertiary amine compounds remain unaffected. Other adducts are $\text{ScX}_3 \cdot 2\text{py}$ and $\text{ScX}_3 \cdot 4\text{pip}$ ($\text{X} = \text{Cl}, \text{Br}$), which are white solids that dissolve in nonpolar organic solvents (433, 434). On the other hand, the compounds $\text{ScCl}_3 \cdot 3(o\text{-phen})$, $\text{ScCl}_3 \cdot 2(2,2'\text{-bipy})$, and $\text{ScCl}_3 \cdot 2(4,4'\text{-bipy})$ ($o\text{-phen} = 1,10\text{-phenanthroline}$; $\text{bipy} = \text{bipyridine}$) are 1:3 electrolytes in aqueous solution and thus

TABLE VII
FORMATION CONSTANTS OF ACETYLACETONE CHELATES

Cation	Metal ion concn.,	Log K_1	Log K_2	Log K_3
	$M \times 10^3$			
Sc ³⁺	10	8.0	7.2	Ppt.
Y ³⁺	1	6.4	4.7	2.8
La ³⁺	10	5.1	3.9	2.8

TABLE VIII
ABSORPTION SPECTRA OF ACETYLACETONATES

Compound	Solvent	—Maximum— absorption,		ϵ , l. mole ⁻¹ cm. ⁻¹
		$m\mu$	cm. ⁻¹	
Sc(acac) ₃	CHCl ₃	297	33,700	28,800
	C ₂ H ₅ OH ^a	296 ^a	33,800 ^a	35,500 ^a
Y(acac) ₃	CHCl ₃	282	35,500	25,900
La(acac) ₃	CHCl ₃	275	36,400	24,900

^a From ref. 24; other data from ref. 236.

probably contain chelated arrangements (249). The neutral complex Sc(bipy)₃ has been reported as a black, crystalline reduction product of a reaction with dilithium bipyridine (215). Its magnetic moment of 1.99 Bohr magnetons suggests the presence of a single unpaired electron with a small contribution from orbital coupling.

Although a normal oxalate, Sc₂(C₂O₄)₃·6H₂O, has been described (280, 543, 596), reaction with excess oxalate ion has led to the isolation of at least the following substances: K₃Sc₂(C₂O₄)₃·4H₂O, NH₄Sc(C₂O₄)₂·2H₂O, KSc(C₂O₄)₂·2H₂O, NaSc(C₂O₄)₂·3H₂O, Na₄Sc₂(C₂O₄)₅·9H₂O, Na₃Sc(C₂O₄)₃·6H₂O, and K₃Sc(C₂O₄)₃ (543, 583). Many of these compositions suggest a coordination number of six for the ion Sc³⁺, and indeed the ion [Sc(C₂O₄)₃]³⁻ has been reported to exist in solution (596, 618). Scandium oxalate, solubility product constant = 4.0×10^{-28} g.-ion⁵ l.⁻⁵ at 25° (513), gives the compound [Sc(NH₃)₆]₂(C₂O₄)₃ with gaseous ammonia (596). The succinate resembles the succinates of yttrium and the yttrium earth metals most closely (618). Solubilities of the rhodizonates change in the order La³⁺ > Nd³⁺ > Y³⁺ > Yb³⁺ > Sc³⁺ (6).

Phenylphosphonic acid has been found to give a precipitate Sc(C₆H₅PO₃)₃·3H₂O with scandium ion but not with the rare earth metal ions in the presence of tartaric and citric acids (3). Scandium and cerium(IV) ions form polymeric complex species with di(2-ethylhexyl)-phosphoric acid, which reagent extracts both scandium nitrate and chloride into toluene (421). Many polyphosphates, among them inositol pyrophosphate (phytin) and adenosine triphosphate, precipitate scandium ion without forming soluble complexes (34, 36, 37).

Among the inner complexes, the acetylacetonate is the best known. Formation-constant data at 30.0° and zero ionic strength, as summarized in Table VII (255), indicate an increase in thermodynamic stability in the series La³⁺-Y³⁺-Sc³⁺. Although the 3-carbon in the

acetylacetonate moiety of the scandium chelate can be brominated without destruction of the compound (283), tracer studies have shown that in chloroform solution there is 100% exchange in 10 min. with labeled acetylacetonate (282). The lability of the ligand-Sc³⁺ bond thus compares well with that of the ligand-Ln³⁺ bond observed for the methoxyacetylacetonate chelates in the water-dioxane mixed solvent system (464), even though the scandium chelate is the most stable in terms of free energy of formation data.

Scandium acetylacetonate has a crystal structure that differs from that of the analogous rare earth metal compounds (18, 258). Although the solution absorption spectra of scandium and yttrium acetylacetonates are nearly identical (382), there are some differences in the carbonyl charge-transfer bands that may reflect differences in bonding. The decrease in wave length of maximum absorption, as shown in Table VIII, may be explained on the basis of a decreased delocalization of ligand electron density as a consequence of the more diffuse character of the 4d_π and 5d_π metal orbitals of yttrium and lanthanum in comparison with the 3d_π orbitals of scandium (236). The change in ϵ is explained similarly. Infrared data indicate an increase in M³⁺-O bond strength from the rare earth metal ion to scandium ion chelates (118). This conclusion is supported by the observation that scandium acetylacetonate can be sublimed, whereas the others decompose on being heated. The precipitation of a hydroxobis(acetylacetonato)scandium complex (Table VII) illustrates again the affinity of this cation for hydroxide groups.

With scandium ion, 8-quinolinol forms the water-insoluble compound Sc(C₉H₆NO)₃·HC₉H₆NO (443). Yttrium and the rare earth metal ions are precipitated under comparable conditions (444). Investigations of the scandium compound by infrared (584), thermogravimetric (584, 613-617), chemical (584), and ultraviolet (373) means have resulted in conflicting views as to the role of the adduct molecule of 8-quinolinol in the structure. Estimates that the strength of the bond holding this molecule is *ca.* 1 kcal./mole (446) are in accord with the view that it is held by lattice forces (443, 446, 584), but the possibility of direct coordination to give an entity H[Sc(On)₄] cannot be completely eliminated, since titrimetric studies in acetonitrile indicate that all four 8-quinolinol groups are equivalent (585). Pyrolysis gives no indication of the formation of a 3:1 compound (616). No comparable 4:1 compound has been reported for yttrium on the lanthanides.

Scandium, yttrium, and the rare earth metal ions give only 3:1 chelates with 7-(α -anilino)benzyl-8-quinolinol (437). These ions also react with 2,5-dihydroxy-1,4-benzoquinone (445).

Although the compounds (C₂H₅)₃Sc·O(C₂H₅)₂ and (C₂H₅)₃Y·O(C₂H₅)₂ have been reported (442), their ex-

istence has been questioned (1). Tris(cyclopentadienyl)scandium, $\text{Sc}(\text{C}_5\text{H}_5)_3$, is salt-like, as are its lanthanide analogs (47, 505, 625).

2. Applications

The scandium-containing complexes have been used most commonly either to separate scandium ion from other closely-related species or to identify and determine this ion (246). Differences between the stabilities of the scandium species and those of the other cations are usually the bases for such applications.

a. Solvent Extraction

This technique is useful for separating scandium from yttrium and the rare earth elements. Thus, scandium is efficiently separated by preferentially removing the latter elements from a nonaqueous nitrate-tri-*n*-butyl phosphate system with 6 *M* hydrochloric acid solution (420). Extraction of 6–8 *M* hydrochloric or nitric acid solutions with tri-*n*-butyl phosphate or the di-*n*-butyl derivatives of tetraethylene glycol is useful for separating scandium from the above elements and thorium (430). Distribution coefficients for scandium and yttrium ion for tri-*n*-butyl phosphate are, respectively, 0.04 and <0.001 for a 3.0 *M* aqueous hydrochloric acid phase and 50 and 0.05 for an 8.0 *M* hydrochloric acid phase (430). The extraction of the ions Sc^{3+} , Y^{3+} , and La^{3+} into amyl alcohol solutions of mono-alkylphosphoric acids (H_2RPO_4 , where R = propyl, butyl, amyl, hexyl, octyl) from aqueous nitric acid solutions suggests (Table IX) formation of the species $\text{Sc}(\text{HRPO}_4)_3$, $\text{HY}(\text{HRPO}_4)_4$, and $\text{HLa}(\text{HRPO}_4)_4$ (607).

Scandium nitrate solutions, unlike those of yttrium and the rare earth metal nitrates, can be extracted with diethyl ether (53). Extraction is more effective in the presence of thiocyanate ion (52, 146, 147). At an aqueous-phase pH below 5.8, scandium is selectively removed from the rare earth elements by extraction of its *N*-benzoylphenylhydroxylamine complex into butanol, amyl alcohol, isoamyl alcohol, amyl acetate, chloroform, or benzene (4). The reddish-violet complexes of scandium and the tripositive rare earth metal ions with glyoxal bis(2-hydroxyanil) are all extractable into amyl alcohol or quinoline, but the scandium complex is the most stable (398). The complexes of these cations with 1-(2-pyridylazo)-2-naphthol extract into diethyl ether, carbon tetrachloride, chloroform, or benzene (502). The corresponding salicylates are also extractable (553). Scandium can be removed from mixtures with the rare earth metal ions by extraction into chloroform from aqueous perchlorate solutions using β -isopropyltropolone (124). Extraction of the 8-quinolinol chelates is not selective (598).

The acetylacetonate chelate of scandium has been extracted quantitatively into ethyl acetate from aqueous

solutions at pH 4.5 (598). Benzoylacetone (535) and thenoyltrifluoroacetone (498) behave similarly. The latter compound permits selective extraction of scandium from uranium (11). Mixtures of 1,3-diketones and polyaminopolycarboxylic acids have shown promise for improved separations (128, 129).

b. Ion Exchange

Scandium ion follows lutetium ion in cation-exchange position (101), but it appears before thorium ion in anion exchange (165). Scandium has been completely separated from erbium by adsorption on an anion-exchange resin from a 13 *M* hydrochloric acid solution (645). Adsorption from chloride media on an anion exchanger followed by elution with absolute ethanol selectively removes scandium from yttrium (624). The presence of MCl_4^- species on the column has been suggested. Anion-exchange separation from the rare earth metal ions in general has been reported (299). Scandium is adsorbed from 0.1 *M* hydrochloric acid–1 *M* hydrofluoric acid solution, but aluminum, yttrium, and europium ions are not (392). From 0.025–8.0 *M* thiocyanate solutions, scandium is readily adsorbed on an anion-exchanger (583). Adsorbability is altered by the presence of ethylenediamine-*N,N,N',N'*-tetraacetate (391).

Aminopolycarboxylate ions in general remove scandium from a cation exchanger prior to the rare earth elements (220, 254). Oxalic acid solutions effect the same separation (276), as do hydrofluoric acid solutions (163) and buffered (pH 2.7–3.0) citric acid solutions (253, 461). Elution from a cation-exchange resin with phosphoric acid has been reported to remove scandium ion selectively, in keeping with the observation that four-membered rings formed from the PO_4^{3-} group require a metal ion of radius 0.7 Å. for maximum stability (174). Removal of scandium ion from such a column with perchloric acid is a consequence of ion-pair formation (174). Adsorption followed by elution of the species $\text{Sc}(\text{SCN})_2\text{Cl}$ with an ammonium thiocyanate–hydrochloric acid mixture has been reported to separate scandium effectively from the cerium earths but not from the yttrium earths (200). Elution with α -hydroxyisobutyric acid solution as the temperature of the column was slowly decreased from 95 to 35° has been reported as improving the separation of scandium from the rare earth metal ions (546).

c. Chromatographic Adsorption

The successful separation of scandium from the rare earth metal and thorium ions by selective hydrolysis of the nitrates in contact with silica gel has been described (309). Exceptionally pure scandium has been obtained from mixtures containing the rare earths by adsorption

TABLE IX
PAPER CHROMATOGRAPHY DATA

Cation	R_f value		
	Solvent A ^a	Solvent B ^a	Solvent C ^a
Sc ³⁺	0.97	1.00	0.57
Y ³⁺	0.59	0.58	...
La ³⁺	0.31	0.40	...
Ce ³⁺	0.38	0.46	...
Pr ³⁺	0.38	0.51	...
Nd ³⁺	0.22	0.54	...
Sm ³⁺	0.47	0.55	0.39 (av.)
Eu ³⁺	0.49	0.55	...
Gd ³⁺	0.43	0.56	...
Dy ³⁺	0.62	0.62	...
Ho ³⁺	0.56
Er ³⁺	0.60	0.64	...
Yb ³⁺	0.59
Ac ³⁺	0.08

^a Solvent A: 1-butanol-acetylacetone-acetic acid-water, 20:6:1:13 (316); solvent B: methyl acetate, R_f values relative (263); solvent C: Nitrate solution on paper saturated with 7 M LiNO₃-2 M HNO₃ (102).

on cellulose columns and elution with aqueous nitric acid (74).

As indicated by the R_f values summarized in Table IX (102, 263, 316), paper chromatography can be used effectively to separate small quantities of scandium ion from the rare earth metal ions. Scandium ion moves faster, by a sizable factor, than any other related cation. Paper electrophoresis of 0.1% citric acid solutions indicates very slow movement of the scandium band and thus very strong complexing of that ion (315). Results with 8-quinolinol in acetic acid are comparable (214). In the presence of nitrohydroxylamine the ions Sc³⁺, La³⁺, and Ce³⁺ all migrate to the positive pole (588).

d. Quantitative Determination

The principles and practice of certain chelatometric methods for determining both scandium and the rare earth elements have been reviewed (152). A number of colored complexes of scandium ion serve as titrimetric indicators. For example, murexide is useful in nitrilotriacetate titrations (33); 3-hydroxy-4-[(1-hydroxy-2-naphthyl)azo]-7-nitro-1-naphthalenesulfonic acid (Eriochrome Black T) (636), PAN (83), 2-(2-pyridylazo)chromotropic acid (515), 2-(2-pyridylazo)-1-amino-8-hydroxy-3,6-naphthalenedisulfonic acid (515), PAR (515), and Xylenol Orange (277, 284, 464) in ethylenediamine-N,N,N',N'-tetraacetate titrations; and Eriochrome Black T in malic acid titrations (637). Both direct and back titration procedures have been described.

Colorimetric determinations involving chelating agents are sensitive for scandium and the rare earth metal ions but often lack specificity. Thus, Acid Chrome Pure Blue V can be used for all ions at concentrations of 0.005-0.5 mg./ml. (500). 2,2'-[(1,8-Di-

hydroxy-3,6-disulfo-2,7-naphthalene)bis(azo)]dibenzene-arsenic acid (Arsenazo III) gives blue species absorbing at 695 and 605 m μ with the rare earth metal ions at pH 1.5-3.5 and a violet species absorbing at 562 and 675 m μ with scandium ion at the same pH (480). Beer's law is obeyed over the range 0.4-2 γ /ml. Other Arsenazo dyes have been useful in both photometric (308, 310, 340) and titrimetric (164) techniques. Bis-[4-hydroxy-3-(8-amino-1-hydroxydisulfo-2-naphthyl-azophenyl)sulfone (Sulfonazo) gives a violet-blue complex with scandium ion that permits determinations at 0.2 γ /5 ml. (65). The 1:2 scandium complex with glyoxal bis(2-hydroxyanil) permits determinations of this cation in ethanol-water mixtures at pH 4.5-5.5 in the presence of limited quantities of the ions Y³⁺, La³⁺, and Nd³⁺ but not in the presence of the ions Ce³⁺, Ce⁴⁺, and Er³⁺ (399). The colorless complex of scandium ion with Tiron absorbs strongly at 310 m μ and thus provides a sensitive, but not selective, basis for photometric determination (202). Methods based upon 5-[α -(3-carboxy-5-methyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2,6-dichlorobenzyl]-2,3-cresotic acid (Pontachrome Azure Blue B) (503), PAR (516), and 1,2-dihydroxyanthraquinone (alizarin) (11) have been described also.

The dyes Acid Chrome Dark Blue ZK, Acid Chrome Blue-Black, Acid Chrome Blue K, Acid Chrome Dark Blue, Permanent Red 4 B, Acid Chrome Bordeaux 5, and Purpurin all form fluorescent chelates with scandium ion, but no correlation between observed fluorescence and color is apparent (291). Other compounds giving fluorescent species with scandium are 2',3,4',5,7-pentahydroxyflavone (Morin) (30), alizarin sulfonate (30), 8-quinolinols (289, 544), salicylaldehyde semicarbazide (290), and resorcyaldehyde (237). Scandium complexes appear to fluoresce more strongly than the rare earth metal complexes (30). Fluorescence is most intense when the metal ion contains filled shells and may be quenched by strongly paramagnetic species (e.g., Gd³⁺ added to Nd³⁺) or appropriate electronic transitions (e.g., Yb³⁺) (544). Mineral acids enhance the fluorescence of scandium compounds (30).

Colored chelates, such as those with aurintricarboxylate ion (478), cochineal (31, 81, 619), or carminic acid (71), have been used to detect both scandium and the rare earth metal ions.

V. RELATIONSHIP TO ACTINIDE CHEMISTRY

A. INTRODUCTION

Complex species formed by the actinide ions (atomic numbers 89-103) are often similar to those formed by the lanthanide ions. The actinides do differ from the lanthanides in the predominance of stable higher oxidation states in the Th-Pu region (170, 180, 270), but among the heavier elements (Am-Lw), the tripositive

state becomes the most stable in aqueous solution and in most solid-state compounds. Americium(III), unlike its electronic analog europium(III), is not reducible to the dipositive state but is oxidizable to the tetrapositive state (13). Curium(IV) also exists. Thus, the most direct comparisons in coordination chemistry really involve actinium and the heaviest actinides. Even among the latter some differences are to be expected because the 5f orbitals are more available for bonding than the 4f orbitals (270). Reviews describing the general coordination chemistry of the actinides (92, 170, 270) are available. Ion-exchange (547) and solvent-extraction (270) procedures that depend upon complex formation have been described. Other useful summaries deal with protactinium (62), americium and curium (418), the transuranium elements in general (488, 489), and spectrophotometric studies of americium species in solution (640). The monograph by Katz and Seaborg (270) is particularly informative.

B. SOME COMPARISONS OF COMPLEXES OF THE ACTINIDES WITH THOSE OF THE LANTHANIDES

1. Electronic Structure and Spectra

The absorption spectra of the anhydrous solids UCl_4 , NpCl_4 , PuCl_3 , and AmX_3 ($\text{X} = \text{Cl}, \text{Br}$) at room temperature consist of sharply defined, line-like bands that are clustered in groups and are thus closely comparable with those of rare earth compounds. The crystal absorption spectrum of the ion Am^{3+} is comparable only to that of the ion Eu^{3+} in sharpness of bands (160). Comparable sharply defined spectra have been obtained for the salts AmCl_3 and CfCl_3 in an LaCl_3 lattice (194, 195). The spectra of the ions Am^{3+} and Cm^{3+} in aqueous solution show considerable solvent dependence in that although the absorption bands remain narrow, they are intensified over those of the corresponding lanthanide ions (77, 548).

Spectral data indicate that the most readily involved electrons among the actinide species are in the 5f orbitals (160), which are less well shielded than the 4f orbitals (261). This decrease in screening accounts for the enhanced ligand-field effects observed among the complexes of the actinides. Observed $5f^n \rightarrow 5f^{n-1}6d^1$ transitions in the spectra of protactinium(V), uranium(III), and neptunium(III) suggest that the 5f electrons in the ground state are outside the emanation shells (265). The absorption spectra of complexes of uranium(IV) and of plutonium(VI) fluoride indicate interelectronic repulsion parameters only ca. 60% of those of the corresponding lanthanides, whereas the Landé factors are about twice as large. The presence of 5f electrons does not necessarily influence the constancy of tervalency noted among the heavier members of the series (265). Observed ligand field effects in absorption spectra have prompted the proposal that bonding

in the complexes of the actinide ions involves 5f orbitals (180).

2. Solid Complex Species

The coprecipitation of americium(III) and europium(III) with lanthanum oxalate gives a crystallization coefficient of 4.9 for the former and 3.8 for the latter (186). Hydrated plutonium(III) and americium(III) oxalates, like cerium(III) oxalate but unlike the oxalates of the other tripositive rare earth metal ions, give the dioxides at 320° in air rather than the anhydrous compounds (178).

The carbonato, sulfato, and acetato complexes of both cerium(IV) and uranium(IV) are examples of coordination number eight, with the coordination shell being filled by either water or the acido groups (181). In binuclear species, the sulfato group may be bridging (181). Coordination number eight is characteristic also of the acetylacetonates of cerium(IV), thorium(IV), and uranium(IV) (184, 185). Each of these solids exists in two crystalline forms, α and β (185). The same coordination number is found with the polymeric uranium(IV) complex with dioctylpyrophosphate ion (183). The geometry is probably the square antiprism arrangement that is characteristic of thorium acetylacetonate (183). This uranium(IV) chelate is dimeric in dioctylpyrophosphoric acid-ligroin solutions.

A number of fluoro complexes, particularly of the tetrapositive ions, have been described (13, 304, 649). Although structural data are lacking, it has been shown by phase studies that both cerium(III) and plutonium(III) form incongruently melting species of the type NaMF_4 (26). Cases of isomorphism among the halides of the actinides and lanthanides are well known (159, 564).

3. Complex Species in Solution

Hydrolysis of the americium(III) ion, as typical, begins at pH 4.5 (534). The observed enhanced thermodynamic stabilities of the chloro complexes of Pu^{3+} and Cm^{3+} (605) and of Am^{3+} (189, 605) over those of the analogous rare earth metal ions is a reflection of participation of 5f orbitals in bonding (106). Ion-exchange data (section VIIC2) suggest comparable behaviors of the tripositive ions of both the actinides and lanthanides with various chelating agents (270). Thermodynamic stabilities increase, of course, with increasing cationic charge. Thus, the formation constant of the thorium(IV) chelate with ethylenediamine-N,N,N',N'-tetraacetic acid is larger than those for the ions Ln^{3+} , but of about the same magnitude as that for Sc^{3+} (406).

The R_f values for the ions Pu^{3+} , Pu^{4+} , PuO_2^{2+} , and Am^{3+} , as determined by partition chromatography with

TABLE X

DISTRIBUTION OF TERVALENT IONS BETWEEN WATER AND TOLUENE IN THE PRESENCE OF THENOYLTRIFLUOROACETONE AT 25° AND pH 3.4

Cation	Distribution coefficient ^a	Cation	Distribution coefficient ^a
Eu ³⁺	0.82	Bk ³⁺	4.15
Yb ³⁺	5.59	Cf ³⁺	2.20
Ac ³⁺	0.0001	Es ³⁺	1.60
Am ³⁺	0.29	Fm ³⁺	2.58
Cm ³⁺	0.24		

^a Concentration in toluene divided by concentration in aqueous phase.

a 1-butanol-nitric acid medium, vary directly with nitric acid concentration and, when compared with those for UO₂²⁺, Th⁴⁺, La³⁺, Ce³⁺, Nd³⁺, Pm³⁺, Sm³⁺, Eu³⁺, and Gd³⁺, indicate that any mixture of these ions can be chromatographically separated (90). Under electrophoretic conditions, actinium is more rapidly transported toward the cathode in a 1% citric acid solution than either lanthanum or scandium (317), thus indicating the reduced stability of the actinium chelate.

C. APPLICATIONS

1. Solvent Extraction

Probably as a consequence of enhanced stability of the resulting chelates, thorium(IV) can be separated from the tripositive lanthanides by preferential extraction into chloroform or hexane in the presence of salicylic, 3,5-dinitrobenzoic, or cinnamic acid (223). Similar separations involving both the ions Th⁴⁺ and UO₂²⁺ have been effected with tropolones (122), azines (559), 1-nitroso-2-naphthol (125), 2-nitroso-1-naphthol (125), and phosphate esters (424). Thenoyltrifluoroacetone preferentially removes thorium from Th⁴⁺-Ac³⁺ mixtures (199). The relative basicities of the trivalent cations are indicated by the solvent-extraction data in Table X (332). The abrupt change between the ions Cm³⁺ and Bk³⁺ shows clearly that more than mere change in cationic radius is involved.

Americium(III) is more readily separated from lanthanum than from either yttrium or promethium by the use of hydroxamic acid (574). With β -isopropyltropolone, the ions Eu³⁺ and Am³⁺ are roughly comparable in their distribution between water and chloroform, but with 5,7-dichloro-8-quinolinol, a stronger base, extraction of americium(III) is favored (127).

Yttrium ion can be separated from Am³⁺, Cm³⁺, and Bk³⁺ by extraction with di-*n*-butyl-, di-2-ethylhexyl-, or 4-(1,1,3,3-tetramethylbutyl)phenylphosphoric acid (424). Linearity with atomic number of log *K* values for the tri-*n*-butyl phosphate complexes is observed for both the tripositive actinides and lanthanides, giving parallel behavior in solvent extraction studies. These log *K* values are roughly the same for Am³⁺ and Pm³⁺.

TABLE XI

SEPARATION FACTORS RELATIVE TO Cm³⁺

Cation	Separation factor	Cation	Separation factor
Y ³⁺	0.06		
Eu ³⁺	0.41	Am ³⁺	1.45 (0.99) ^a
Gd ³⁺	0.29	Cm ³⁺	1.00
Tb ³⁺	0.14	Bk ³⁺	0.45
Dy ³⁺	0.075	Cf ³⁺	0.20
Ho ³⁺	0.046	Es ³⁺	0.13
Er ³⁺	0.038	Fm ³⁺	0.069
Tm ³⁺	0.029	Md ³⁺	0.050
Yb ³⁺	0.022	No ³⁺	0.038
Lu ³⁺	0.16		

^a In parentheses, ref. 650; others, ref. 169.

For the ions Y³⁺, Ce³⁺, and Am³⁺, the species extracted from aqueous nitric acid have the formula M(NO₃)₃·3-TBP, whereas for Ce⁴⁺, Th⁴⁺, Np⁴⁺, and Pu⁴⁺ they have the formula M(NO₃)₄·2TBP (211).

It is apparent that a given tripositive actinide ion resembles closely the tripositive lanthanide ion of comparable radius in solvent-extraction behavior. In each series, the ion with a half-filled *f* shell (Gd³⁺ and Cm³⁺) is less well extracted than would be expected from the behaviors of its neighbors (41). When solvent extractability of the lanthanides and actinides is compared for acidic aqueous solutions (>6 *M* HNO₃), ionic radius is an important criterion. At lower acidities, the trends are different. Thus, there is a minimum in extractability at Cm³⁺ among the actinides but a maximum around Gd³⁺ among the lanthanides (41).

2. Ion Exchange

Americium(III) and curium(III) have been separated from both the rare earth metal ions and each other by adsorption on a cation exchanger and selective alternate elution with ammonium citrate and fluorosilicate solutions (572). Elution with ammonium thiocyanate solution has given gram-quantity separations of americium(III) from the lanthanides (91). Actinium can be separated from lanthanum by selective elution from a cation exchanger with buffered citric acid solution (330, 579, 641). Thorium(IV) has been separated from the tripositive actinides and lanthanides by either anion (293) or cation (550, 589) exchange. Cerium(IV) does not interfere. Cation exchange has been used also to separate uranium from the lanthanides (459).

The quantitative separation of americium(III) and curium(III) from tripositive cerium, promethium, and lutetium by selective elution of the former with hydrochloric acid solutions has been reported (549). The separation involves chloro complexes of the actinide species (106). No separation of americium from curium was achieved.

The elution curves of complexes of the trans-plutonium elements fall into the expected positions. The order Bk³⁺-Cm³⁺-Am³⁺ conforms to the order Tb³⁺-

Gd³⁺-Eu³⁺ (571). Californium (III) appears close to dysprosium (549), and americium(III) elutes nearly simultaneously with promethium in the lactate system. Chelating agents that give five-membered rings containing the metal ion are the most efficient eluting agents (179). It is of interest that nearly equal separation factors (Table XI) characterize the pairs No³⁺-Er³⁺, Md³⁺-Ho³⁺, Fm³⁺-Dy³⁺, Es³⁺-Tb³⁺, Cf³⁺-Gd³⁺, and Bk³⁺-Eu³⁺ in elutions with α -hydroxyisobutyric acid solutions (86, 169, 650).

Elution studies using thiocyanate ion and an anion exchanger have shown the thiocyanatoamericium(III) complex to be more stable than the corresponding promethium complex by *ca.* 1.3 kcal./mole (554). The existence in solution of anionic thiocyanato (554) and chloro (106) complexes of the actinide ions has been established.

D. CONCLUSION

Direct comparisons of the behaviors of the heaviest actinides with the lanthanides are complicated by the necessity for studying the former on no more than a tracer scale and sometimes on only a "few-atom" scale. Although this complication necessitates extensive extrapolation, the evidence is sufficient to demonstrate the validity of a "lanthanide analogy." Complications induced as a consequence of enhanced covalency among the actinide complexes suggest that the actinide ions may give species that are unknown with the lanthanides and that can be used to advantage to separate the two series from each other. Until more species of this type than are currently known have been described, it is reasonable to use data for the lanthanides to predict behaviors of the actinides in comparable oxidation states.

VIII. REFERENCES

- (1) Afanas'ev, B. N., and Tsyganova, P. A., *J. Gen. Chem. USSR*, **18**, 306 (1948).
- (2) Aksel'rud, N. V., *Ukr. Khim. Zh.*, **27**, 431 (1961).
- (3) Alimarin, I. P., Fadeeva, V. I., and Petrova, T. N., *Zh. Analit. Khim.*, **16**, 549 (1961).
- (4) Alimarin, I. P., and Tsze, Y.-S., *Zavodsk. Lab.*, **25**, 1435 (1959).
- (5) Allred, A. L., and Rochow, E. G., *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).
- (6) Al-Mahdi, A. A. K., and Schönfeld, T., *Mikrochim. Acta*, **254** (1962).
- (7) Almeida, I. G., and Danon, J., *Anal. Assoc. Brasil Quim.*, **19**, 133 (1960); *Chem. Abstr.*, **56**, 9501b (1962).
- (8) Anderegg, G., *Helv. Chim. Acta*, **43**, 825 (1960).
- (9) Anderegg, G., Nägeli, P., Müller, F., and Schwarzenbach, G., *Helv. Chim. Acta*, **42**, 827 (1959).
- (10) Andreeva, Z. F., and Kolosov, I. V., *Izv. Timiryazev. Sel'skokhoz. Akad.*, No. 1, 212 (1962); *Chem. Abstr.*, **58**, 63h (1963).
- (11) Ashbrook, A. W., *Analyst*, **88**, 113 (1963).
- (12) Asher, D. R., Hansen, R. D., Seamster, A. H., Small, H., and Wheaton, R. M., *Ind. Eng. Chem. Process Design Develop.*, **1**, 52 (1962).
- (13) Asprey, L. B., "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 58-65.
- (14) Asprey, L. B., Ellinger, F. H., Fried, S., and Zachariasen, W. H., *J. Am. Chem. Soc.*, **79**, 5825 (1957).
- (15) Asprey, L. B., and Keenan, T. K., *J. Inorg. Nucl. Chem.*, **16**, 260 (1961).
- (16) Astakhov, K. V., Verenikin, V. B., and Zimin, V. I., *Zh. Neorgan. Khim.*, **6**, 2077 (1961).
- (17) Astakhov, K. V., Verenikin, V. B., Zimin, V. I., and Zver'kova, A. D., *Zh. Neorgan. Khim.*, **6**, 2069 (1961).
- (18) Astbury, W. T., *Proc. Roy. Soc. (London)*, **A112**, 448 (1926).
- (19) Augur, V., LaFontaine, L., and Caspar, C., *Compt. rend.*, **180**, 376 (1925).
- (20) Axtmann, R. C., *J. Chem. Phys.*, **30**, 340 (1959).
- (21) Babko, A. K., and Dubovenko, L. I., *Zh. Neorgan. Khim.*, **2**, 808 (1957).
- (22) Baker, L. C. W., Gallagher, G. A., and McCutcheon, T. P., *J. Am. Chem. Soc.*, **75**, 2493 (1953).
- (23) Banks, C. V., Hensinkveld, M. R., and O'Laughlin, J. W., *Anal. Chem.*, **33**, 1235 (1961).
- (24) Bardet, L., and Brun, C., *Bull. soc. chim. France*, 1877 (1962).
- (25) Barnum, D. W., *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).
- (26) Barton, C. J., Redman, J. D., and Strehlow, R. A., *J. Inorg. Nucl. Chem.*, **20**, 45 (1961).
- (27) Batyayev, I. M., Larionov, S. V., and Shul'man, V. M., *Zh. Neorgan. Khim.*, **6**, 153 (1961).
- (28) Bayer-Helms, F., *Z. Naturforsch.*, **13a**, 161 (1958).
- (29) Bear, J. L., Choppin, G. R., and Quagliano, J. V., *J. Inorg. Nucl. Chem.*, **24**, 1601 (1962).
- (30) Beck, G., *Mikrochim. Acta*, **2**, 9 (1937).
- (31) Beck, G., *Mikrochemie*, **27**, 47 (1939).
- (32) Beck, G., *Helv. Chim. Acta*, **29**, 357 (1946).
- (33) Beck, G., *Anal. Chim. Acta*, **1**, 69 (1947).
- (34) Beck, G., *Mikrochemie ver. Mikrochim. Acta*, **34**, 62 (1948).
- (35) Beck, G., *Mikrochemie ver. Mikrochim. Acta*, **33**, 344 (1948).
- (36) Beck, G., *Anal. Chim. Acta*, **4**, 21 (1950).
- (37) Beck, G., *Mikrochemie ver. Mikrochim. Acta*, **36/37**, 790 (1951).
- (38) Beck, G., and Gasser, A., *Anal. Chim. Acta*, **3**, 41 (1949).
- (39) Belyaev, Yu. I., *Spektral'n. Opred. Redkikh i Rasseyan. Elementov, Akad. Nauk SSSR, Inst. Geokhim. i Analit. Khim.*, 125 (1962); *Chem. Abstr.*, **57**, 11,832 (1962).
- (40) Berg, T., and Becker, E., *Z. anal. Chem.*, **119**, 1 (1940).
- (41) Best, G. F., Hesford, E., and McKay, H. A. C., *J. Inorg. Nucl. Chem.*, **12**, 136 (1959).
- (42) Bethe, H., *Ann. Physik*, **3**, 133 (1929).
- (43) Betts, R. H., private communication, 1960.
- (44) Betts, R. H., and Dahlinger, O. F., *Can. J. Chem.*, **37**, 91 (1959).
- (45) Bhat, A. N., and Jain, B. D., *J. Indian Chem. Soc.*, **38**, 327 (1961).
- (46) Biedermann, G., Kilpatrick, M., Pokras, L., and Sillén, L. G., *Acta Chem. Scand.*, **10**, 1327 (1956).
- (47) Birmingham, J. M., and Wilkinson, G., *J. Am. Chem. Soc.*, **78**, 42 (1956).
- (48) Bjerrum, J., Schwarzenbach, G., and Sillén, L. G., "Stability Constants. Part I. Organic Ligands," The Chemical Society, London, 1957.
- (49) Bjerrum, J., Schwarzenbach, G., and Sillén, L. G., "Stability Constants. Part II. Inorganic Ligands," The Chemical Society, London, 1958.
- (50) Blatz, L. A., *J. Phys. Chem.*, **66**, 160 (1962).
- (51) Bobtelsky, M., and Graus, B., *J. Am. Chem. Soc.*, **77**, 1990 (1955).
- (52) Bock, R., *Z. anal. Chem.*, **133**, 110 (1951).

- (53) Bock, R., and Bock, E., *Naturwissenschaften*, **36**, 344 (1949).
- (54) Bock, R., and Meyer, K. H., *Chem. Ingr.-Tech.*, **25**, 141 (1953).
- (55) Bommer, H., and Hohmann, E., *Z. anorg. allgem. Chem.*, **248**, 373 (1941).
- (56) Borisenko, L. F., *Tr. Inst. Mineralog., Geokhim. i Kristallokhim. Redkikh Elementov, Voprosy Mineral., Akad. Nauk SSSR, Geokhim. i Genezisa Mestorozhdeniĭ Redkikh Elementov*, **2**, 78 (1959); *Chem. Abstr.*, **54**, 19,357h (1960).
- (57) Boulanger, F., *Ann. chim. (Paris)*, **7**, 733 (1952).
- (58) Brady, G. W., *J. Chem. Phys.*, **33**, 1079 (1961).
- (59) Brantley, J. C., Doctoral Dissertation, University of Illinois, 1949.
- (60) Bril, K., Bril, S., and Krumholz, P., *J. Phys. Chem.*, **63**, 256 (1959).
- (61) Brimm, E. O., Doctoral Dissertation, University of Illinois, 1940.
- (62) Brown, D., and Maddock, A. G., *Quart. Rev.*, (London), **17**, 289 (1963).
- (63) Brown, W. B., Pope, G. W., Steinbach, J. F., and Wagner, W. F., *J. Inorg. Nucl. Chem.*, **25**, 4 (1963).
- (64) Brown, W. B., Steinbach, J. F., and Wagner, W. F., *J. Inorg. Nucl. Chem.*, **13**, 119 (1960).
- (65) Brudz, V. G., and Drapkina, D. A., *Sb. Statei, Vses. Nauchn.-Issled. Inst. Khim. Reaktivov i Osobo Chistykh Khim. Veshchestv*, **24**, 60 (1961); *Chem. Abstr.*, **57**, 1539g (1962).
- (66) Brunisholz, G., *Helv. Chim. Acta*, **38**, 455 (1955).
- (67) Brunisholz, G., *Helv. Chim. Acta*, **38**, 1654 (1955).
- (68) Brunisholz, G., *Chimia*, **11**, 97 (1957).
- (69) Brunisholz, G., *Helv. Chim. Acta*, **40**, 2004 (1957).
- (70) Brunisholz, G., and Cohen, R., *Helv. Chim. Acta*, **41**, 188 (1958).
- (71) Brunisholz, G., and Cohen, R., *Helv. Chim. Acta*, **41**, 460 (1958).
- (72) Brunisholz, G., and Randin, M., *Helv. Chim. Acta*, **41**, 195 (1958).
- (73) Bruno, M., and Barbieri, R., *Gazz. chim. ital.*, **91**, 1055 (1961).
- (74) Burstall, F. H., Davies, G. R., Linstead, R. P., and Wells, R. A., *Nature*, **163**, 64 (1949).
- (75) Busev, A. I., and Fan, C., *Talanta*, **9**, 101 (1962).
- (76) Callahan, C. M., Fernelius, W. C., and Block, B. P., *Anal. Chim. Acta*, **16**, 101 (1957).
- (77) Carnall, W. T., and Fields, P. R., *J. Am. Chem. Soc.*, **81**, 4445 (1959).
- (78) Carnall, W. T., Gruen, D. M., and McBeth, R. L., *J. Phys. Chem.*, **66**, 2159 (1962).
- (79) Cefola, M., Tompa, A. S., Celiano, A. V., and Gentile, P. S., *Inorg. Chem.*, **1**, 290 (1962).
- (80) Cerrai, I. E., Testa, C., and Triulzi, C., *Energie Nucl.*, **9**, 193 (1962); *Chem. Abstr.*, **57**, 6654 (1962).
- (81) Charlot, G., *Anal. Chim. Acta*, **1**, 218 (1947).
- (82) Cheng, K. L., *Chemist-Analyst*, **47**, 93 (1958).
- (83) Cheng, K. L., and Williams, T. R., Jr., *Chemist-Analyst*, **44**, 96 (1955).
- (84) Choppin, G. R., *J. Chem. Educ.*, **36**, 462 (1959).
- (85) Choppin, G. R., and Chopoorian, J. A., *J. Inorg. Nucl. Chem.*, **22**, 97 (1961).
- (86) Choppin, G. R., Harvey, B. G., and Thompson, S. G., *J. Inorg. Nucl. Chem.*, **2**, 66 (1956).
- (87) Choppin, G. R., and Silva, R. J., *J. Inorg. Nucl. Chem.*, **3**, 153 (1956).
- (88) Choppin, G. R., and Unrein, P. J., *J. Inorg. Nucl. Chem.*, **25**, 387 (1963).
- (89) Chopoorian, J. A., Doctoral Dissertation, Florida State University, 1961.
- (90) Clanet, F., *J. Chromatog.*, **7**, 373 (1962).
- (91) Coleman, J. S., Penneman, R. A., Keenan, T. K., LeMar, L. E., Armstrong, D. E., and Asprey, L. B., *J. Inorg. Nucl. Chem.*, **3**, 327 (1956).
- (92) Comyns, A. E., *Chem. Rev.*, **60**, 115 (1960).
- (93) Connick, R. E., and Mattern, R. L., Abstracts, 121st National Meeting of the American Chemical Society, 1952, p. 35N.
- (94) Connick, R. E., and Mayer, S. W., *J. Am. Chem. Soc.*, **73**, 1176 (1951).
- (95) Conway, J. G., Gruber, J. B., Hulet, E. K., Morrow, R. J., and Gutmacher, R. G., *J. Chem. Phys.*, **36**, 189 (1962).
- (96) Courtney, R. C., Gustafson, R. L., Chaberek, S., Jr., and Martell, A. E., *J. Am. Chem. Soc.*, **80**, 2121 (1958).
- (97) Cromer, D. T., and Kline, R. J., *J. Am. Chem. Soc.*, **76**, 5282 (1954).
- (98) Crouthamel, C. E., and Martin, D. S., Jr., *J. Am. Chem. Soc.*, **72**, 1382 (1950).
- (99) Crouthamel, C. E., and Martin, D. S., Jr., *J. Am. Chem. Soc.*, **73**, 569 (1951).
- (100) Danon, J., *J. Inorg. Nucl. Chem.*, **5**, 237 (1958).
- (101) Danon, J., *J. Inorg. Nucl. Chem.*, **7**, 422 (1958).
- (102) Danon, J., and Levi, M. C., *J. Chromatog.*, **3**, 193 (1960).
- (103) Davidenko, N. K., *Zh. Neorgan. Khim.*, **4**, 2469 (1959).
- (104) Davidenko, N. K., *Zh. Neorgan. Khim.*, **7**, 2709 (1962).
- (105) Dergunov, E. P., *Dokl. Akad. Nauk SSSR*, **85**, 1025 (1952).
- (106) Diamond, R. M., Street, K., and Seaborg, G. T., *J. Am. Chem. Soc.*, **76**, 1461 (1954).
- (107) Dismukes, J. P., Jones, L. H., and Bailar, J. C., Jr., *J. Phys. Chem.*, **65**, 792 (1961).
- (108) Dragulescu, C., Simonescu, T., Menessy, I., and Anton, R., *Acad. Rep. Populare Romine, Baza Cercetari Stiint. Timisoara, Studii Cercetari, Stiinta Chim.*, **8**, 9 (1961); *Chem. Abstr.*, **57**, 399a (1962).
- (109) Dutt, N. K., *J. Indian Chem. Soc.*, **26**, 405 (1949); **27**, 191 (1950).
- (110) Dutt, N. K., *J. Indian Chem. Soc.*, **28**, 533 (1951).
- (111) Dutt, N. K., and Bandyopadhyay, P., *Sci. Cult. (Calcutta)*, **22**, 690 (1957).
- (112) Dutt, N. K., and Bandyopadhyay, P., *Sci. Cult. (Calcutta)*, **23**, 105 (1957).
- (113) Dutt, N. K., and Bandyopadhyay, P., *Sci. Cult. (Calcutta)*, **23**, 365 (1958).
- (114) Dutt, N. K., and Bandyopadhyay, P., *Sci. Cult. (Calcutta)*, **27**, 403 (1961).
- (115) Dutt, N. K., and Goswami, N., *J. Indian Chem. Soc.*, **30**, 275 (1953).
- (116) Dutt, N. K., and Gupta, A. K., *J. Indian Chem. Soc.*, **29**, 105 (1952).
- (117) Dutt, N. K., and Mukherjee, H. G., *J. Indian Chem. Soc.*, **30**, 272 (1953).
- (118) Duval, C., Freymann, R., and Lecomte, J., *Bull. soc. chim. France*, 106 (1952).
- (119) Duyckaerts, G., and Drize, P., *Bull. soc. chim. Belges*, **71**, 306 (1962).
- (120) Duyckaerts, G., Drize, P., and Simon, A., *J. Inorg. Nucl. Chem.*, **13**, 332 (1960).
- (121) Dyrssen, D., *Svensk. Kem. Tidskr.*, **66**, 234 (1954).
- (122) Dyrssen, D., *Acta Chem. Scand.*, **9**, 1567 (1955).
- (123) Dyrssen, D., *Acta Chem. Scand.*, **15**, 1614 (1961).
- (124) Dyrssen, D., *Trans. Roy. Inst. Technol. Stockholm*, **188**, 3 (1962).
- (125) Dyrssen, D., Dyrssen, M., and Johansson, E., *Acta Chem. Scand.*, **10**, 106 (1956).

- (126) Dyrssen, D., Dyrssen, M., and Johansson, E., *Acta Chem. Scand.*, **10**, 341 (1956).
- (127) Dyrssen, D., Heffez, M., and Sekine, T., *J. Inorg. Nucl. Chem.*, **16**, 367 (1961).
- (128) Dziomko, V. M., *Dokl. Akad. Nauk SSSR*, **133**, 106 (1960).
- (129) Dziomko, V. M., *Dokl. Akad. Nauk SSSR*, **134**, 1091 (1960).
- (130) Edge, R. A., *J. Chromatog.*, **5**, 526 (1961).
- (131) Edge, R. A., *J. Chromatog.*, **6**, 452 (1961).
- (132) Eliazyan, L. A., and Tarayan, V. M., *Izv. Akad. Nauk Arm. SSR, Khim. Nauki*, **14**, No. 2, 127 (1961); *Chem. Abstr.*, **56**, 9694 (1962).
- (133) Elliot, R. J., and Stevens, K. W. H., *Proc. Roy. Soc. (London)*, **A219**, 387 (1953).
- (134) Ephraim, F., *Ber.*, **61**, 80 (1928).
- (135) Ephraim, F., and Bloch, R., *Ber.*, **59**, 2692 (1926).
- (136) Ephraim, F., and Bloch, R., *Ber.*, **61**, 65 (1928).
- (137) Ephraim, F., and Bloch, R., *Ber.*, **61**, 72 (1928).
- (138) Ephraim, F., and Rây, P., *Ber.*, **62**, 1509 (1929).
- (139) Ephraim, F., and Rây, P., *Ber.*, **62**, 1520 (1929).
- (140) Ephraim, F., and Rây, P., *Ber.*, **62**, 1639 (1929).
- (141) Erämetsä, O., *Suomen Kemistilehti*, **B17**, 30 (1944).
- (142) Feibush, A. M., Rowley, K., and Gordon, L., *Anal. Chem.*, **30**, 1610 (1958).
- (143) Feng, R. K., and Fernando, Q., *Anal. Chim. Acta*, **24**, 548 (1961).
- (144) Fialkov, Ya. A., and Ermolenko, V. I., *Zh. Neorgan. Khim.*, **4**, 1369 (1959).
- (145) Fidelis, I., and Siekierski, S., *J. Chromatog.*, **5**, 161 (1961).
- (146) Fischer, W., and Bock, R., *Z. anorg. allgem. Chem.*, **249**, 146 (1942).
- (147) Fischer, W., Steinhäuser, O., Hohmann, E., Bock, E., and Borchers, P., *Z. anal. Chem.*, **133**, 57 (1951).
- (148) Fischer, W., and Werner, H. E., *Z. anorg. allgem. Chem.*, **312**, 221 (1961).
- (149) Fischer, W., Wernet, J., and Zumbusch-Pfisterer, M., *Z. anorg. allgem. Chem.*, **258**, 157 (1949).
- (150) Fitch, F. T., and Russell, D. S., *Can. J. Chem.*, **29**, 363 (1951).
- (151) Fitzwater, D. R., and Rundle, R. E., *Z. Krist.*, **112**, 362 (1959).
- (152) Flaschka, H., Barnard, A. J., Jr., and Broad, W. C., *Chemist-Analyst*, **47**, 78 (1958).
- (153) Fomin, V. V., Kartushova, R. E., and Rudenko, T. I., *Zh. Neorgan. Khim.*, **3**, 2117 (1958).
- (154) Fowles, G. W. A., *Proc. Symp. Chem. Co-ord. Compds., Agra, India, 1960*, part 2, 41 (1961); *Chem. Abstr.*, **55**, 11,166c (1961).
- (155) Freasier, B. F., Oberg, A. G., and Wendlandt, W. W., *J. Phys. Chem.*, **62**, 700 (1958).
- (156) Freed, S., Weissmann, S. I., and Fortress, F. E., *J. Am. Chem. Soc.*, **63**, 1079 (1941).
- (157) Freiling, E. C., and Bunney, L. R., *J. Am. Chem. Soc.*, **76**, 1021 (1954).
- (158) Freiser, H., *Analyst*, **77**, 830 (1952).
- (159) Fried, S., Hagemann, F. T., and Zachariasen, W. H., *J. Am. Chem. Soc.*, **72**, 771 (1950).
- (160) Fried, S., and Leitz, F. J., Jr., *J. Chem. Phys.*, **17**, 540 (1949).
- (161) Fritz, J. J., Field, P. E., and Grenthe, I., *J. Phys. Chem.*, **65**, 2070 (1961).
- (162) Fritz, J. J., Grenthe, I., Field, P. E., and Fernelius, W. C., *J. Am. Chem. Soc.*, **82**, 6199 (1960).
- (163) Fritz, J. S., Garralda, B. B., and Karraker, S. K., *Anal. Chem.*, **33**, 882 (1961).
- (164) Fritz, J. S., and Pietrzyk, D. J., *Anal. Chem.*, **31**, 1157 (1959).
- (165) Fritz, J. S., and Pietrzyk, D. J., *Talanta*, **8**, 143 (1961).
- (166) Fritz, J. S., Richard, M. J., and Lane, W. J., *Anal. Chem.*, **30**, 1776 (1958).
- (167) Fronaeus, S., *Svensk Kem. Tidskr.*, **65**, 19 (1953).
- (168) Fuger, J., *J. Inorg. Nucl. Chem.*, **18**, 263 (1961).
- (169) Galti, R. C., Phillips, L., Sikkeland, T., Muga, M. L., and Thompson, S. G., *J. Inorg. Nucl. Chem.*, **11**, 251 (1959).
- (170) Gel'man, A. D., Moskvina, A. I., Zaitsev, L. M., and Mefod'eva, M. P., "Complex Compounds of Transuranium Elements," translated by C. N. Turton and T. I. Turton, Consultants Bureau, New York, N. Y., 1962.
- (171) Geller, S., *Acta Cryst.*, **10**, 713 (1957).
- (172) Gelles, E., and Nancollas, G. H., *Trans. Faraday Soc.*, **52**, 98 (1956).
- (173) Gelles, E., and Nancollas, G. H., *Trans. Faraday Soc.*, **52**, 680 (1956).
- (174) Genge, J. A. R., and Salmon, J. E., *J. Chem. Soc.*, 1459 (1959).
- (175) Giesbrecht, E., *J. Inorg. Nucl. Chem.*, **15**, 265 (1960).
- (176) Giesbrecht, E., and Audrieth, L. F., *J. Inorg. Nucl. Chem.*, **6**, 308 (1958).
- (177) Giesbrecht, E., and Perrier, M., *Anal. Assoc. Brasil. Quim.*, **19**, 121 (1960); *Chem. Abstr.*, **56**, 13,747 (1962).
- (178) Glasner, A., and Steinberg, M., *Bull. Res. Council Israel*, **A8**, 174 (1959).
- (179) Glass, R. A., *J. Am. Chem. Soc.*, **77**, 807 (1955).
- (180) Glueckauf, E., and McKay, H. A. C., *Nature*, **165**, 594 (1950).
- (181) Golovnya, V. A., Pospelova, L. A., and Bolotova, G. T., *Zh. Neorgan. Khim.*, **5**, 2204 (1960).
- (182) Gordon, L., and Shaver, K. J., *Anal. Chem.*, **25**, 784 (1953).
- (183) Grdenić, D., and Korpar, B., *J. Inorg. Nucl. Chem.*, **12**, 149 (1959).
- (184) Grdenić, D., and Matković, B., *Croat. Chem. Acta*, **30**, 95 (1958); *Chem. Abstr.*, **54**, 1015 (1960).
- (185) Grdenić, D., and Matković, B., *Acta Cryst.*, **12**, 817 (1959).
- (186) Grebenshchikova, V. I., and Bryzgalova, R. V., *Radio-khimiya*, **2**, No. 2, 152 (1960).
- (187) Grenthe, I., *J. Am. Chem. Soc.*, **83**, 360 (1961).
- (188) Grenthe, I., *Acta Chem. Scand.*, **16**, 1695 (1962).
- (189) Grenthe, I., *Acta Chem. Scand.*, **16**, 2300 (1962).
- (190) Grenthe, I., private communication, 1962.
- (191) Grenthe, I., and Fernelius, W. C., *J. Am. Chem. Soc.*, **82**, 6258 (1960).
- (192) Grenthe, I., and Fernelius, W. C., "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 12-25.
- (193) Gromova, M. I., Varaksina, I. F., and Peshkova, V. M., *Vestn. Mosk. Univ., Ser. Mat., Mekhan., Astron., Fiz. Khim.*, **13**, No. 6, 171 (1958); *Chem. Abstr.*, **53**, 15,756a (1959).
- (194) Gruber, J. B., *J. Chem. Phys.*, **35**, 2186 (1961).
- (195) Gruber, J. B., and Conway, J. G., *J. Chem. Phys.*, **36**, 191 (1962).
- (196) Gruen, D. M., *J. Inorg. Nucl. Chem.*, **4**, 74 (1957).
- (197) Guit, R., and Gruen, D. M., *J. Inorg. Nucl. Chem.*, **21**, 259 (1961).
- (198) Gupta, A. K., and Powell, J. E., *Inorg. Chem.*, **1**, 955 (1962).
- (199) Hagemann, F. T., U. S. Patent 2,632,763; *Chem. Abstr.*, **47**, 7914 (1953).
- (200) Hamaguchi, H., Kuroda, R., Aoki, K., Sugishita, R., and Onuma, N., *Talanta*, **10**, 153 (1963).
- (201) Hamaguchi, H., Kuroda, R., and Onuma, N., *Talanta*, **10**, 120 (1963).

- (202) Hamaguchi, H., Onuma, N., Kuroda, R., and Sugishita, R., *Talanta*, **9**, 563 (1962).
- (203) Harder, R., and Chaberek, S., *J. Inorg. Nucl. Chem.*, **11**, 197 (1959).
- (204) Hardwick, T. J., and Robertson, E., *Can. J. Chem.*, **29**, 818 (1951).
- (205) Hardwick, T. J., and Robertson, E., *Can. J. Chem.*, **29**, 828 (1951).
- (206) Harrington, G., and Sundheim, B. R., *Ann. N. Y. Acad. Sci.*, **79**, 950 (1960); *Chem. Abstr.*, **54**, 16,170 (1960).
- (207) Hartmann, H., and Lorenz, E., *Z. Elektrochem.*, **54**, 341 (1950).
- (208) Healy, T. V., *J. Inorg. Nucl. Chem.*, **19**, 314 (1961).
- (209) Healy, T. V., *J. Inorg. Nucl. Chem.*, **19**, 328 (1961).
- (210) Healy, T. V., and McKay, H. A. C., *Trans. Faraday Soc.*, **52**, 633 (1956).
- (211) Healy, T. V., and McKay, H. A. C., *Rec. trav. chim.*, **75**, 730 (1956).
- (212) Heidt, L. J., and Berestecki, J., *J. Am. Chem. Soc.*, **77**, 2049 (1955).
- (213) Helmholtz, L., *J. Am. Chem. Soc.*, **61**, 1544 (1939).
- (214) Herrero-Lancina, M., *J. Chromatog.*, **2**, 438 (1959).
- (215) Herzog, S., Byhan, G., and Wulfert, P., *Z. Chem.*, **1**, 370 (1961).
- (216) Herzog, S., and Gustav, K., *Z. Naturforsch.*, **17b**, 62 (1962).
- (217) Hesford, E., Jackson, E. E., and McKay, H. A. C., *J. Inorg. Nucl. Chem.*, **9**, 279 (1959).
- (218) Higgins, G. H., and Street, K., *J. Am. Chem. Soc.*, **72**, 5321 (1950).
- (219) Hiller, M. A., Doctoral Dissertation, Iowa State University, 1959.
- (220) Hiller, M. A., and Powell, J. E., U. S. Atomic Energy Commission Report IS300 (1959).
- (221) Hoard, J. L., private communication, 1964.
- (222) Hoard, J. L., Smith, G. S., and Lind, M., "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 296-302.
- (223) Hök-Bernström, B., *Svensk. Kem. Tidskr.*, **68**, 34 (1956).
- (224) Holleck, L., *Z. Naturforsch.*, **2b**, 81 (1947).
- (225) Holleck, L., *Oesterr. Chemiker-Ztg.*, **60**, 65 (1959).
- (226) Holleck, L., and Eckardt, D., *Naturwissenschaften*, **40**, 409 (1953).
- (227) Holleck, L., and Eckardt, D., *Z. Naturforsch.*, **8a**, 660 (1953).
- (228) Holleck, L., and Eckardt, D., *Z. Naturforsch.*, **9a**, 347 (1954).
- (229) Holleck, L., and Eckardt, D., *Z. Naturforsch.*, **9b**, 274 (1954).
- (230) Holleck, L., and Eckardt, D., *Z. Elektrochem.*, **59**, 202 (1955).
- (231) Holleck, L., and Hartinger, L., *Angew. Chem.*, **66**, 586 (1954).
- (232) Holleck, L., and Hartinger, L., *Angew. Chem.*, **68**, 411 (1956).
- (233) Holleck, L., and Liebold, G., *Naturwissenschaften*, **44**, 583 (1957).
- (234) Holleck, L., and Sölla, K., *Naturwissenschaften*, **47**, 442 (1960).
- (235) Holloway, J. H., and Reilley, C. N., *Anal. Chem.*, **32**, 249 (1960).
- (235a) Holm, L. W., Choppin, G. R., and May, D., *J. Inorg. Nucl. Chem.*, **19**, 251 (1961).
- (236) Holm, R. H., and Cotton, F. A., *J. Am. Chem. Soc.*, **80**, 5658 (1958).
- (237) Holzbecher, Z., *Collection Czech. Chem. Commun.*, **25**, 977 (1960).
- (238) Hoppe, R., *Angew. Chem.*, **71**, 45 (1959).
- (239) Hoppe, R., and Liebe, W., *Z. anorg. allgem. Chem.*, **313**, 221 (1961).
- (240) Hoppe, R., and Roedder, K. M., *Z. anorg. allgem. Chem.*, **312**, 277 (1961).
- (241) Hoppe, R., and Roedder, K. M., *Z. anorg. allgem. Chem.*, **313**, 154 (1961).
- (242) Horwitz, E. P., Doctoral Dissertation, University of Illinois, 1957.
- (243) Huffman, E. H., and Oswalt, R. L., *J. Am. Chem. Soc.*, **72**, 3323 (1950).
- (244) Hunt, E. B., Rundle, R. E., and Stosick, A. J., *Acta Cryst.*, **7**, 106 (1956).
- (245) Ichikawa, F., *Bull. Chem. Soc. Japan*, **34**, 183 (1961).
- (246) Irving, H., *Quart. Rev. (London)*, **5**, 200 (1951).
- (247) Isaac, N. M., Fields, P. R., and Gruen, D. M., *J. Inorg. Nucl. Chem.*, **21**, 152 (1961).
- (248) Ivanov-Emin, B. N., Nisel'son, L. A., and Ivolgina, A. T., *Zh. Neorgan. Khim.*, **5**, 2841 (1960).
- (249) Ivanov-Emin, B. N., Nisel'son, L. A., and Larionova, L. A., *Zh. Neorgan. Khim.*, **6**, 334 (1961).
- (250) Ivanov-Emin, B. N., and Ostroumov, E. A., *J. Gen. Chem. USSR*, **14**, 772 (1944).
- (251) Ivanov-Emin, B. N., and Ostroumov, E. A., *Zh. Neorgan. Khim.*, **4**, 71 (1959).
- (252) Iwase, A., *Nippon Kagaku Zasshi*, **81**, 1486 (1960); *Chem. Abstr.*, **56**, 8069a (1962).
- (253) Iya, V. K., *Compt. rend.*, **236**, 608 (1953).
- (254) Iya, V. K., and Loriers, J., *Compt. rend.*, **237**, 1413 (1953).
- (255) Izatt, R. M., Fernelius, W. C., Haas, C. G., Jr., and Block, B. P., *J. Phys. Chem.*, **59**, 170 (1955).
- (256) Izatt, R. M., Haas, C. G., Jr., Block, B. P., and Fernelius, W. C., *J. Phys. Chem.*, **58**, 1133 (1954).
- (257) Jackson, D. E., Doctoral Dissertation, University of Illinois, 1950.
- (258) Jaeger, F. M., *Verslag Akad. Wetenschap.*, **22**, 1188 (1914).
- (259) James, R. A., and Bryan, W. B., *J. Am. Chem. Soc.*, **76**, 1982 (1954).
- (260) James, R. A., Powell, J. E., and Spedding, F. H., *J. Inorg. Nucl. Chem.*, **19**, 133 (1961).
- (261) Jezowska-Trzebiatowska, B., and Bukietynska, K., *J. Inorg. Nucl. Chem.*, **19**, 38 (1961).
- (262) Jicha, D. C., Bachelor's Dissertation, University of Illinois, 1955.
- (263) Johnson, O. H., and Krause, H. H., *Anal. Chim. Acta*, **11**, 128 (1954).
- (263a) Jones, M. M., *Science*, **121**, 371 (1955).
- (264) Jørgensen, C. K., *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.*, **30**, No. 22 (1956).
- (265) Jørgensen, C. K., *Mol. Phys.*, **2**, 96 (1959).
- (266) Jørgensen, C. K., "Progress in Inorganic Chemistry," Vol. 4, F. A. Cotton, Ed., Interscience Publishers, New York, N. Y., 1962, pp. 73-124.
- (267) Jørgensen, C. K., "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962, Chapter 11.
- (268) Jura, G., and Grotz, L., *Anal. Chem.*, **23**, 1044 (1951) (abstract cited therein).
- (269) Karraker, R. H., Doctoral Dissertation, Iowa State University, 1962.
- (270) Katz, J. J., and Seaborg, G. T., "The Chemistry of the Actinide Elements," John Wiley and Sons, Inc., New York, N. Y., 1957.
- (271) Kawashima, T., Ogawa, H., and Hamaguchi, H., *Talanta*, **8**, 552 (1961).
- (272) Ketelaar, J. A. A., *Physica*, **4**, 619 (1937).

- (273) Ketelle, B. H., and Boyd, G. E., *J. Am. Chem. Soc.*, **73**, 1862 (1951).
- (274) Kharitonov, Ya. Ya., Orlovskii, V. P., and Tananaev, I. V., *Zh. Neorgan. Khim.*, **8**, 1093 (1963).
- (275) Kilpatrick, M., and Pokras, L., *J. Electrochem. Soc.*, **100**, 85 (1953).
- (276) Kimura, K., Ikeda, N., Kimura, K., Kawaniski, H., Kimura, M., and Suzuki, I., *Radioisotopes* (Tokyo), **9**, 108 (1960).
- (277) Kinnunen, J., and Wennerstrand, B., *Chemist-Analyst*, **46**, 92 (1957).
- (278) Kirmse, E. M., *Z. Chem.*, **1**, 332 (1961).
- (279) Kirmse, E. M., *Z. Chem.*, **1**, 334 (1961).
- (280) Klein, M. J., and Bernays, P. M., *J. Am. Chem. Soc.*, **73**, 1364 (1951).
- (281) Klemm, W., and Krose, E., *Z. anorg. Chem.*, **253**, 218 (1947).
- (282) Kluiber, R. W., *J. Am. Chem. Soc.*, **82**, 4839 (1960).
- (283) Kluiber, R. W., U. S. Patent 3,014,939; *Chem. Abstr.*, **57**, 14,708f (1962).
- (284) Körbl, J., Přibil, R., and Emr, A., *Collection Czech. Chem. Commun.*, **22**, 961 (1957).
- (285) Kolat, R. S., Doctoral Dissertation, Iowa State University, 1962.
- (286) Kolat, R. S., and Powell, J. E., *Inorg. Chem.*, **1**, 293 (1962).
- (287) Kolat, R. S., and Powell, J. E., *Inorg. Chem.*, **1**, 485 (1962).
- (288) Kolosova, G. M., and Senyavich, M. M., *Redkozem. Elementy, Akad. Nauk SSSR, Inst. Geokhim. Analit. Khim.*, **138** (1958); *Chem. Abstr.*, **54**, 20,611h (1960).
- (289) Korenman, I. M., and Avrova, N. F., *Tr. Khim. i Khim. Tekhnol.*, **1**, 138 (1958); *Chem. Abstr.*, **54**, 6393h (1960).
- (290) Korenman, I. M., and Efimychev, V. S., *Zh. Analit. Khim.*, **17**, 425 (1962).
- (291) Korenman, I. M., and Starostin, G. P., *Izv. Vysshikh. Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, **4**, 561 (1961); *Chem. Abstr.*, **56**, 13,531 (1962).
- (292) Korenman, I. M., Tumanov, A. A., and Sorokina, V. M., *Izv. Vysshikh. Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, **3**, 580 (1960); *Chem. Abstr.*, **55**, 1163 (1961).
- (293) Korkisch, J., and Tera, F., *Anal. Chem.*, **33**, 1264 (1961).
- (294) Korpusov, C. V., Levin, V. I., Brezhneva, N. E., Prokhovova, N. P., Eskevich, I. V., and Serechenko, P. M., *Russ. J. Inorg. Chem.*, **7**, 1167 (1962).
- (295) Kostromina, N. A., *Ukr. Khim. Zh.*, **26**, 3 (1960); *Chem. Abstr.*, **54**, 16,252 (1960).
- (296) Kostromina, N. A., *Ukr. Khim. Zh.*, **26**, 299 (1960); *Chem. Abstr.*, **55**, 4230 (1961).
- (297) Kostromina, N. A., *Zh. Neorgan. Khim.*, **7**, 1559 (1962).
- (298) Kostromina, N. A., *Radiokhimiya*, **4**, 167 (1962).
- (299) Kraus, K. A., Nelson, F., and Smith, G. W., *J. Phys. Chem.*, **58**, 11 (1954).
- (300) Kriss, E. E., and Sheka, Z. A., *Dokl. Akad. Nauk SSSR*, **138**, 846 (1961).
- (301) Kruger, P., and Coryell, C. D., *J. Chem. Educ.*, **32**, 280 (1955).
- (302) Krumholz, P., *J. Phys. Chem.*, **63**, 1313 (1959).
- (303) Krumholz, P., "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 564-570.
- (304) Kruse, F. H., and Asprey, L. B., *Inorg. Chem.*, **1**, 137 (1962).
- (305) Kurry, J. W., U. S. Atomic Energy Commission Report UCRL2271 (1953).
- (306) Kurry, J. W., Hugus, Z. Z., and Latimer, W. M., *J. Phys. Chem.*, **61**, 1021 (1957).
- (307) Kurry, J. W., Paul, A. D., Hepler, L. G., and Connick, R. E., *J. Am. Chem. Soc.*, **81**, 4185 (1959).
- (308) Kuteĭnikov, A. F., *Zavodsk. Lab.*, **24**, 1050 (1960); *Chem. Abstr.*, **54**, 15,069d (1960).
- (309) Kuteĭnikov, A. F., and Brodskaya, V. M., *Zh. Analit. Khim.*, **17**, 305 (1962).
- (310) Kuznetsov, V. I., *J. Gen. Chem. USSR*, **14**, 897 (1944).
- (311) Laidler, K. J., and Pegis, C., *Proc. Roy. Soc. (London)*, **A241**, 80 (1957).
- (312) Lane, T. J., and Quinlan, K. P., *J. Am. Chem. Soc.*, **82**, 2997 (1960).
- (313) Lawson, K. E., *Spectrochim. Acta*, **17**, 248 (1961).
- (314) Leal, R. S., *J. Inorg. Nucl. Chem.*, **10**, 159 (1959).
- (315) Lederer, M., *Compt. rend.*, **236**, 200 (1953).
- (316) Lederer, M., *Compt. rend.*, **236**, 1557 (1953).
- (317) Lederer, M., *Anal. Chim. Acta*, **11**, 145 (1954).
- (318) Lewis, W. B., Jackson, J., Lemons, J. F., and Taube, H., *J. Chem. Phys.*, **36**, 694 (1962).
- (319) Levy, S. C., and Powell, J. E., U. S. Atomic Energy Commission Report IS-421 (1961).
- (320) Linz, A., Jr., U. S. Patent 3,009,774; *Chem. Abstr.*, **56**, 11,228 (1962).
- (321) Lohr, H. R., and Cunningham, B. B., *J. Am. Chem. Soc.*, **73**, 2025 (1951).
- (322) Lories, J., *Compt. rend.*, **240**, 1537 (1955).
- (323) Lories, J., and Carminati, D., *Compt. rend.*, **237**, 1328 (1953).
- (324) Lories, J., and Lenoir, C., *Compt. rend.*, **247**, 468 (1958).
- (325) Lories, J., and Tuesnu, J., *Compt. rend.*, **239**, 1643 (1955).
- (326) Mackey, J. L., Doctoral Dissertation, Iowa State Univ., 1961.
- (327) Mackey, J. L., Hiller, M. A., and Powell, J. E., *J. Phys. Chem.*, **66**, 311 (1962).
- (328) Mackay, J. L., Powell, J. E., and Spedding, F. H., *J. Am. Chem. Soc.*, **84**, 2047 (1962).
- (329) McClure, D. S., "Solid State Physics," Vol. 9, Academic Press, New York, N. Y., 1959, p. 399.
- (330) McLane, C. K., and Peterson, S., "The Transuranium Elements," G. T. Seaborg, J. J. Katz, and W. M. Manning, Ed., Part II, McGraw-Hill Book Co., New York, N. Y., 1949, p. 1385.
- (331) Magin, R. E., Manastyrskiy, S., and Dubeck, M., *J. Am. Chem. Soc.*, **85**, 627 (1963).
- (332) Magnusson, L. B., and Anderson, M. L., *J. Am. Chem. Soc.*, **76**, 6207 (1954).
- (333) Manning, P. G., and Monk, C. B., *Trans. Faraday Soc.*, **58**, 938 (1962).
- (334) Marcus, Y., and Nelson, F., *J. Phys. Chem.*, **63**, 77 (1959).
- (335) Marezio, M., Plettinger, H. A., and Zachariasen, W. H., *Acta Cryst.*, **14**, 234 (1961).
- (336) Marsh, J. K., *J. Chem. Soc.*, 1972 (1934).
- (337) Marsh, J. K., *J. Chem. Soc.*, 554 (1939).
- (338) Marsh, J. K., *J. Chem. Soc.*, 577 (1950).
- (339) Marsh, J. K., *J. Chem. Soc.*, 1819 (1950).
- (340) Marsh, J. K., *J. Chem. Soc.*, 1337 (1951).
- (341) Marsh, J. K., *J. Chem. Soc.*, 1461 (1951).
- (342) Marsh, J. K., *J. Chem. Soc.*, 3057 (1951).
- (343) Marsh, J. K., *J. Chem. Soc.*, 4804 (1952).
- (344) Marsh, J. K., *J. Chem. Soc.*, 978 (1957).
- (345) Marsh, S. F., Maeck, W. J., Booman, G. L., and Rein, J. E., *Anal. Chem.*, **34**, 1406 (1962).
- (346) Marshall, R. H., Doctoral Dissertation, University of Illinois, 1953.
- (347) Martin, D. S., Jr., Rundle, R. E., and Golden, S. A., *J. Chem. Phys.*, **24**, 1114 (1956).
- (348) Martynenko, L. I., *Zh. Neorgan. Khim.*, **6**, 2704 (1961).
- (349) Martynenko, L. I., Eremin, G. K., and Kamenev, A. I., *Russ. J. Inorg. Chem.*, **4**, 1217 (1959).

- (350) Maslova, G. B., Nazarov, P. P., and Chmutov, K. V., *Zh. Neorgan. Khim.*, **5**, 359 (1960).
- (351) Massart, D. L., and Haste, J., *Anal. Chim. Acta*, **28**, 378 (1963).
- (352) Massonne, J., *Chem. Tech.* (Berlin), **10**, 591 (1958).
- (353) Mayer, S. W., and Freiling, E. C., *J. Am. Chem. Soc.*, **75**, 5647 (1953).
- (354) Mayer, S. W., and Schwartz, S. D., *J. Am. Chem. Soc.*, **72**, 5106 (1950).
- (355) Mayer, S. W., and Schwartz, S. D., *J. Am. Chem. Soc.*, **73**, 222 (1951).
- (356) Mikhailov, V. A., Torgov, V. G., and Melekhina, N. F., *Russ. J. Inorg. Chem.*, **6**, 746 (1961).
- (357) Minczewski, J., and Dybczynski, R., *J. Chromatog.*, **7**, 568 (1962).
- (358) Minczewski, J., and Dybczynski, R., Polish Academy of Sciences, Institute of Nuclear Research, Report 229/VIII (1961).
- (359) Mishchenko, K. P., and Pominov, I. S., *Zh. Fiz. Khim.*, **31**, 2026 (1957).
- (360) Moeller, T., *Record Chem. Progr.* (Hooker-Kresge Sci. Lib.), **14**, 69 (1953).
- (361) Moeller, T., "The Chemistry of the Lanthanides," Reinhold Publishing Corp., New York, N. Y., 1963, Chapters 3 and 4.
- (362) Moeller, T., and Brantley, J. C., *Anal. Chem.*, **22**, 433 (1950).
- (363) Moeller, T., and Brantley, J. C., *J. Am. Chem. Soc.*, **72**, 5447 (1950).
- (364) Moeller, T., and Ferrús, R., *J. Inorg. Nucl. Chem.*, **20**, 261 (1961).
- (365) Moeller, T., and Ferrús, R., *Inorg. Chem.*, **1**, 49 (1962).
- (366) Moeller, T., and Giffin, G., AFOSR Document No. TN-58-589, ASTIA Document No. AD 162113 (1958).
- (367) Moeller, T., Gulyas, E., and Marshall, R. H., *J. Inorg. Nucl. Chem.*, **9**, 82 (1959).
- (368) Moeller, T., and Horwitz, E. P., *J. Inorg. Nucl. Chem.*, **12**, 49 (1959).
- (369) Moeller, T., and Hseu, T.-M., *J. Inorg. Nucl. Chem.*, **24**, 1635 (1962).
- (370) Moeller, T., and Jackson, D. E., *Anal. Chem.*, **22**, 1393 (1950).
- (370a) Moeller, T., and Kremers, H. E., *Chem. Rev.*, **37**, 97 (1945).
- (371) Moeller, T., and Moss, F. A. J., *J. Am. Chem. Soc.*, **73**, 3149 (1951).
- (372) Moeller, T., Moss, F. A. J., and Marshall, R. H., *J. Am. Chem. Soc.*, **77**, 3182 (1955).
- (373) Moeller, T., and Ramaniah, M. V., *J. Am. Chem. Soc.*, **76**, 6030 (1954).
- (374) Moeller, T., and Tecotzky, M., *J. Am. Chem. Soc.*, **77**, 2649 (1955).
- (375) Moeller, T., and Thompson, L. C., *J. Inorg. Nucl. Chem.*, **24**, 499 (1962).
- (376) Moeller, T., Thompson, L. C., and Ferrús, R., "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 3-11.
- (377) Moeller, T., and Ulrich, W. F., *J. Inorg. Nucl. Chem.*, **2**, 164 (1956).
- (378) Moore, F. L., *Anal. Chem.*, **33**, 748 (1961).
- (379) Moore, R. L., and Anderson, R. C., *J. Am. Chem. Soc.*, **67**, 167 (1945).
- (380) Moosath, S. S., and Chandu, S., *J. Inorg. Nucl. Chem.*, **14**, 293 (1960).
- (381) Moosath, S. S., and Rao, M. R. A., *Current Sci.* (India), **25**, 14 (1956).
- (382) Morgan, G. T., and Moss, H. W., *J. Chem. Soc.*, **105**, 189 (1914).
- (383) Morgan, J. C., and James, C., *J. Am. Chem. Soc.*, **36**, 10 (1914).
- (384) Moskal'kova, E. A., and Tolmachev, Yu. M., *Tr. Radiovogo Inst., Khim. i Geokhim.*, **7**, 141 (1956); *Chem. Abstr.*, **51**, 17,549b (1957).
- (385) Moss, F. A. J., Doctoral Dissertation, University of Illinois, 1952.
- (386) Muetterties, E. L., and Castle, J. E., *J. Inorg. Nucl. Chem.*, **18**, 148 (1961).
- (387) Nakatsuka, Y., and Kudo, I., *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 655 (1951).
- (388) Nancollas, G. H., *Quart. Rev.* (London), **14**, 402 (1960).
- (389) Navratil, O., and Kolarik, Z., *Collection Czech. Chem. Commun.*, **26**, 3009 (1961).
- (390) Nazarenko, V. A., and Biryuk, E. A., *Ukr. Khim. Zh.*, **29**, 198 (1963); *Chem. Abstr.*, **59**, 3291g (1963).
- (391) Nelson, F., Day, R. A., Jr., and Kraus, K. A., *J. Inorg. Nucl. Chem.*, **15**, 140 (1960).
- (392) Nelson, F., Rush, R. M., and Kraus, K. A., *J. Am. Chem. Soc.*, **82**, 339 (1960).
- (393) Newton, T. W., and Baker, F. B., *J. Phys. Chem.*, **61**, 934 (1957).
- (394) Noddack, W., and Oertel, G., *Z. Elektrochem.*, **61**, 1216 (1957).
- (395) Nowacki, W., *Naturwissenschaften*, **26**, 801 (1938).
- (396) Nowacki, W., *Z. Krist.*, **101**, 273 (1939).
- (397) Nozaki, T., and Takashima, Y., *Nippon Kagaku Zasshi*, **79**, 1024 (1958); *Chem. Abstr.*, **53**, 8927b (1959).
- (398) Okac, A., and Vrchlabsky, M., *Z. anal. Chem.*, **182**, 425 (1961).
- (399) Okac, A., and Vrchlabsky, M., *Z. anal. Chem.*, **195**, 338 (1963).
- (400) Olivard, J., *Arch. Biochem. Biophys.*, **88**, 382 (1960).
- (401) Onishi, H., and Banks, C. V., *Talanta*, **10**, 399 (1963).
- (402) Onishi, H., Nagai, H., and Toita, Y., *Anal. Chim. Acta*, **26**, 528 (1962).
- (403) Onstott, E. L., *J. Am. Chem. Soc.*, **74**, 3773 (1952).
- (404) Ostroumov, E. A., *Zh. Analit. Khim.*, **3**, 153 (1948).
- (405) Palmer, W. G., "Experimental Inorganic Chemistry," University Press, Cambridge, 1954, p. 72.
- (406) Pan, K., Hseu, T.-M., and Wu, C.-H., *J. Chinese Chem. Soc.* (Taiwan), [II] **6**, 12 (1959).
- (407) Panova, M. G., Brezhneva, N. Ye., and Levin, V. I., *Radiokhimiya*, **2**, 208 (1960).
- (408) Panova, M. G., Levin, V. I., and Brezhneva, N. E., *Radiokhimiya*, **2**, 197 (1960).
- (409) Panova, M. G., Levin, V. I., and Brezhneva, N. E., *Radiokhimiya*, **3**, 52 (1961).
- (410) Paramonova, V. I., Koreichuk, A. S., and Shishlyakov, B. A., *Radiokhimiya*, **1**, 650 (1959).
- (411) Paramonova, V. I., Mosevich, A. N., and Subbotina, A. I., *Zh. Neorgan. Khim.*, **3**, 88 (1958).
- (412) Parker, G. W., and Lantz, P. M., *J. Am. Chem. Soc.*, **72**, 2834 (1950).
- (413) Parry, R. W., "Chemistry of the Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, p. 249.
- (414) Patnaik, D., and Sahoo, B., *Current Sci.* (India), **26**, 355 (1957).
- (415) Patrusheva, E. N., Brezhneva, N. E., and Korpusov, G. V., *Radiokhimiya*, **2**, 541 (1960).
- (416) Paul, A. D., *J. Phys. Chem.*, **66**, 1248 (1962).
- (417) Paul, A. D., Gallo, L. S., and Van Camp, J. B., *J. Phys. Chem.*, **65**, 441 (1961).

- (418) Penneman, R. A., and Asprey, L. B., *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, **7**, 355 (1956).
- (419) Peppard, D. F., Driscoll, W. J., Sironen, R. J., and McCarty, S., *J. Inorg. Nucl. Chem.*, **4**, 326 (1957).
- (420) Peppard, D. F., Faris, J. P., Gray, P. R., and Mason, G. W., *J. Phys. Chem.*, **57**, 294 (1953).
- (421) Peppard, D. F., and Ferraro, J. R., *J. Inorg. Nucl. Chem.*, **10**, 275 (1959).
- (422) Peppard, D. F., Gray, P. R., and Markus, M. M., *J. Am. Chem. Soc.*, **75**, 6063 (1953).
- (423) Peppard, D. F., Horwitz, E. P., and Mason, G. W., *J. Inorg. Nucl. Chem.*, **24**, 429 (1962).
- (424) Peppard, D. F., Mason, G. W., Driscoll, W. J., and McCarty, S., *J. Inorg. Nucl. Chem.*, **12**, 141 (1959).
- (425) Peppard, D. F., Mason, G. W., Driscoll, W. J., and Simen, R. J., *J. Inorg. Nucl. Chem.*, **7**, 276 (1958).
- (426) Peppard, D. F., Mason, G. W., and Hucher, I., *J. Inorg. Nucl. Chem.*, **18**, 245 (1961).
- (427) Peppard, D. F., Mason, G. W., and Hucher, I., *J. Inorg. Nucl. Chem.*, **24**, 881 (1962).
- (428) Peppard, D. F., Mason, G. W., Maier, J. L., and Driscoll, W. J., *J. Inorg. Nucl. Chem.*, **7**, 276 (1958).
- (429) Peppard, D. F., Mason, G. W., and Moline, S. W., *J. Inorg. Nucl. Chem.*, **5**, 141 (1957).
- (430) Peppard, D. F., and Nachtman, E. S., U. S. Patent 2,824,783; *Chem. Abstr.*, **52**, 12,343i (1958).
- (431) Peshkova, V. M., Gromova, L. I., Efrinov, I. P., and Kanaev, N. A., *Redkozem. Elementy Akad. Nauk SSSR, Inst. Geokhim. Analit. Khim.*, 277 (1959); *Chem. Abstr.* **55**, 17,339c (1961).
- (432) Petrů, F., Hájek, B., and Jošt, F., *Croat. Chem. Acta*, **29**, 457 (1957); *Chem. Abstr.*, **52**, 19,665b (1958).
- (433) Petrů, F., and Jošt, F., *Chem. Listy*, **52**, 1645 (1958).
- (434) Petrů, F., and Jošt, F., *Collection Czech. Chem. Commun.*, **24**, 2041 (1959).
- (435) Petrů, F., and Kůtek, F., *Collection Czech. Chem. Commun.*, **25**, 1143 (1960).
- (436) Phillips, D. F., and Deye, J. F., *Anal. Chim. Acta*, **17**, 231 (1957).
- (437) Phillips, J. P., and Duckwall, A. L., *J. Am. Chem. Soc.*, **77**, 5504 (1955).
- (438) Pierce, T. B., and Peck, P. F., *Nature*, **194**, 84 (1962).
- (439) Pierce, T. B., and Peck, P. F., *Nature*, **195**, 597 (1962).
- (440) Pierce, T. B., and Peck, P. F., *Analyst*, **88**, 217 (1963).
- (441) Pirtea, T. I., *Z. anal. Chem.*, **107**, 191 (1936).
- (442) Plets, V. M., *Compt. rend. acad. sci. URSS*, **20**, 27 (1938).
- (443) Pokras, L., and Bernays, P. M., *J. Am. Chem. Soc.*, **73**, 7 (1951).
- (444) Pokras, L., and Bernays, P. M., *Anal. Chem.*, **23**, 757 (1951).
- (445) Pokras, L., and Kilpatrick, M., *Anal. Chem.*, **25**, 1270 (1953).
- (446) Pokras, L., Kilpatrick, M., and Bernays, P. M., *J. Am. Chem. Soc.*, **75**, 1254 (1953).
- (447) Poluektov, N. S., and Kononenko, L. I., *Zh. Neorgan. Khim.*, **6**, 1837 (1961).
- (448) Pollard, F. H., McOnire, J. F. W., and Stevens, H. M., *J. Chem. Soc.*, 4730 (1952).
- (449) Pollard, F. H., McOnire, J. F. W., and Stevens, H. M., *J. Chem. Soc.*, 3435 (1954).
- (450) Pominov, I. S., *Zh. Fiz. Khim.*, **31**, 1926 (1957).
- (451) Pope, G. W., Steinbach, J. F., and Wagner, W. F., *J. Inorg. Nucl. Chem.*, **20**, 304 (1961).
- (452) Popov, A. I., and Wendlandt, W. W., *Anal. Chem.*, **26**, 883 (1954).
- (453) Popov, A. I., and Wendlandt, W. W., *J. Am. Chem. Soc.*, **77**, 857 (1955).
- (454) Powell, J. E., and Farrell, J. L., "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 26-30.
- (455) Powell, J. E., and Mackey, J. L., *Inorg. Chem.*, **1**, 418 (1962).
- (456) Powell, J. E., and Spedding, F. H., *Chem. Eng. Progr. Symp. Ser.*, **55**, 24, 101 (1959).
- (457) Preobrazhenskii, B. K., Kalyamin, A. V., and Lilova, O. M., *Radiokhimiya*, **2**, 239 (1960).
- (458) Purkayastha, B. C., and Pai Verneker, V. R., *Anal. Chem.*, **31**, 814 (1959).
- (459) Purushottam, D., *Current Sci. (India)*, **29**, 308 (1960).
- (460) Quill, L. L., Stites, J. G., and McCarty, C. N., *J. Am. Chem. Soc.*, **70**, 3142 (1948).
- (461) Radhakrishna, P., *Anal. Chim. Acta*, **8**, 140 (1953).
- (462) Radoitchitch, M., *Ann. chim.*, **13**, 5 (1940).
- (463) Ramsay, W. J., Douglas, D. L., and Yost, D. M., *J. Am. Chem. Soc.*, **72**, 2782 (1950).
- (464) Randall, W. J., Doctoral Dissertation, University of Illinois, 1965.
- (465) Randall, W. J., Martin, D. F., and Moeller, T., *Proc. Chem. Soc.*, 340 (1961).
- (466) Reilley, C. N., and Holloway, J. H., *J. Am. Chem. Soc.*, **80**, 2917 (1958).
- (467) Riley, R. F., Doctoral Dissertation, Michigan State University, 1956.
- (468) Roppongi, A., and Kato, T., *Bull. Chem. Soc. Japan*, **35**, 1092 (1962).
- (469) Rossotti, F. J. C., *Discussions Faraday Soc.*, **26**, 191 (1958).
- (470) Rossotti, F. J. C., and Rossotti, H., "The Determination of Stability Constants," McGraw-Hill Book Co., New York, N. Y., 1961.
- (471) Ryabchikov, D. I., and Korchemmaya, E. K., *Dokl. Akad. Nauk SSSR*, **138**, 397 (1961).
- (472) Ryabchikov, D. I., and Terent'eva, E. A., *Compt. rend. acad. sci. URSS*, **51**, 291 (1946).
- (473) Ryabchikov, D. I., Terent'eva, E. A., and Sklyarenko, Yu. S., *Tr. Komis. Analit. Khim., Akad. Nauk SSSR*, **3**, 23 (1951); *Chem. Abstr.*, **47**, 2629a (1953).
- (474) Sacconi, L., and Ercoli, R., *Gazz. chim. ital.*, **79**, 731 (1949).
- (475) Saisho, H., *Bull. Chem. Soc. Japan*, **34**, 859 (1961).
- (476) Saito, N., and Sekine, T., *Nature*, **180**, 753 (1957).
- (477) Sakharova, N. N., *Dokl. Akad. Nauk SSSR*, **113**, 1073 (1957).
- (478) Sarkar, P. B., *Ann. chim.*, [x] **8**, 207 (1927).
- (479) Savitskii, E. M., Terekhova, V. F., and Naumkin, O. P., *Usp. Fiz. Nauk*, **79**, 263 (1963); *Chem. Abstr.*, **59**, 36e (1963).
- (480) Savvin, S. B., and Muk, A. A., *Bull. Inst. Nucl. Sci. "Boris Kidrich" (Belgrade)*, **12**, 97 (1961); *Chem. Abstr.*, **57**, 4029b (1962).
- (481) Sawyer, D. T., and Ambrose, R. T., *Inorg. Chem.*, **1**, 296 (1962).
- (482) Sawyer, D. T., and McKinnie, J. M., *J. Am. Chem. Soc.*, **82**, 4194 (1960).
- (483) Scargill, D., Alcock, K., Fletcher, J. M., Hesford, E., and McKay, H. A. C., *J. Inorg. Nucl. Chem.*, **4**, 304 (1957).
- (484) Schubert, K., and Seitz, A., *Z. anorg. allgem. Chem.*, **256**, 226 (1948).
- (485) Schumann, H., *Z. anorg. allgem. Chem.*, **271**, 29 (1952).
- (486) Schwarzenbach, G., "Advances in Inorganic Chemistry and Radiochemistry," H. J. Emeléus and A. G. Sharpe, Ed., Vol. 3, Academic Press, New York, N. Y., 1961, p. 265.
- (486a) Schwarzenbach, G., and Gut, R., *Helv. Chim. Acta*, **39**, 1589 (1956).
- (487) Schwarzenbach, G., Gut, R., and Anderegg, G., *Helv. Chim. Acta*, **37**, 937 (1954).

- (488) Seaborg, G. T., *Endeavour*, **18**, 5 (1959).
- (489) Seaborg, G. T., "Man-Made Transuranium Elements," Prentice-Hall, Englewood Cliffs, N. J., 1963.
- (490) Seaton, J. A., Sherif, F. G., and Audrieth, L. F., *J. Inorg. Nucl. Chem.*, **9**, 222 (1959).
- (491) Seifer, G. B., *Zh. Neorgan. Khim.*, **4**, 2832 (1959).
- (492) Senyavin, M. M., and Sorochan, A. M., *Zh. Neorgan. Khim.*, **3**, 301 (1958).
- (493) Serdyuk, L. S., *Ukr. Khim. Zh.*, **28**, 786 (1962); *Chem. Abstr.*, **58**, 7420 (1963).
- (494) Serebrennikov, V. V., Ivanova, E. I., and Alekseenko, L. A., *Zh. Neorgan. Khim.*, **4**, 1377 (1959).
- (495) Serebrennikov, V. V., Padalka, M. A., and Levin, I. S., *Uch. Zap. Tomsk. Gos. Univ.*, **26**, 26 (1955); *Chem. Abstr.*, **53**, 12,795c (1959).
- (496) Sheka, Z. A., and Kriss, E. E., *Zh. Neorgan. Khim.*, **6**, 1930 (1961).
- (497) Sheka, Z. A., and Kriss, E. E., *Zh. Neorgan. Khim.*, **7**, 658 (1962).
- (498) Sheperd, E., and Meinke, W. W., U. S. Atomic Energy Commission Report AECU-3879 (1958).
- (499) Shevchenko, V. B., and Smelov, V. S., *Zh. Neorgan. Khim.*, **6**, 732 (1961).
- (500) Sheyanova, F. R., and Malenskaya, V. P., *Trudy po Khim. i Khim. Tekhnol.*, **2**, 560 (1959); *Chem. Abstr.*, **55**, 26,826h (1961).
- (501) Shibata, S., *Anal. Chim. Acta*, **28**, 388 (1963).
- (502) Shibata, S., and Ishiguro, Y., *Nagoya Kogyo Gijutsu Shikensho Hokoku*, **11**, 318 (1962); *Chem. Abstr.*, **57**, 6590 (1962).
- (503) Shigematsu, T., Uesugi, K., and Tabushi, M., *Bunseki Kagaku*, **12**, 267 (1963); *Chem. Abstr.*, **59**, 5765d (1963).
- (504) Shishlovs'kii, O. A., *Nauk. Zap., Kiivs'k. Derzh. Univ.*, **13**, No. 7 (1955); *Zbirnik Fiz. Fak.*, No. 8, 81 (1955); *Chem. Abstr.*, **52**, 9759a (1958).
- (505) Shustrovich, I. E. M., and Dyatkina, M. E., *Zh. Neorgan. Khim.*, **3**, 2721 (1958).
- (506) Shvedov, V. P., and Stepanov, A. V., *Radiokhimiya*, **1**, 162 (1959).
- (507) Siekierski, S., *J. Inorg. Nucl. Chem.*, **12**, 129 (1959).
- (508) Siekierski, S., and Fidelis, I., *J. Chromatog.*, **4**, 60 (1960).
- (509) Sillén, L. G., *Rec. trav. chim.*, **75**, 705 (1956).
- (510) Singh, S., *Z. Krist.*, **105**, 384 (1944).
- (511) Smith, G. W., and Moore, F. L., *Anal. Chem.*, **29**, 448 (1947).
- (512) Smith, H. L., and Hoffman, D. L., *J. Inorg. Nucl. Chem.*, **3**, 243 (1956).
- (513) Sokolov, D. N., *Tr. po Khim. i Khim. Tekhnol.*, **3**, 594 (1960); *Chem. Abstr.*, **56**, 9489 (1962).
- (514) Sokolov, D. N., *Tr. po Khim. i Khim. Tekhnol.*, **55** (1962); *Chem. Abstr.*, **58**, 8453 (1963).
- (515) Sommer, L., and Hnilickova, M., *Naturwissenschaften*, **45**, 544 (1958).
- (516) Sommer, L., and Hnilickova, M., *Anal. Chim. Acta*, **27**, 241 (1962).
- (517) Sonesson, A., *Acta Chem. Scand.*, **12**, 165 (1958).
- (518) Sonesson, A., *Acta Chem. Scand.*, **12**, 1937 (1958).
- (519) Sonesson, A., *Acta Chem. Scand.*, **13**, 998 (1959).
- (520) Sonesson, A., *Acta Chem. Scand.*, **13**, 1437 (1959).
- (521) Sonesson, A., *Acta Chem. Scand.*, **14**, 1495 (1960).
- (522) Sonesson, A., *Acta Chem. Scand.*, **15**, 1 (1961).
- (523) Spedding, F. H., *Discussions Faraday Soc.*, **7**, 214 (1949).
- (524) Spedding, F. H., and Dye, J. L., *J. Am. Chem. Soc.*, **72**, 5350 (1950).
- (525) Spedding, F. H., Fulmer, E. J., Powell, J. E., Butler, T. A., and Yaffe, I. S., *J. Am. Chem. Soc.*, **73**, 4840 (1951).
- (526) Spedding, F. H., and Jaffe, S., *J. Am. Chem. Soc.*, **76**, 882 (1954).
- (527) Spedding, F. H., and Powell, J. E., *J. Am. Chem. Soc.*, **74**, 857 (1952).
- (528) Spedding, F. H., and Powell, J. E., *J. Am. Chem. Soc.*, **76**, 2550 (1954).
- (529) Spedding, F. H., Powell, J. E., Daane, A. H., Hiller, M. A., and Adams, W. A., *J. Electrochem. Soc.*, **105**, 683 (1958).
- (530) Spedding, F. H., Powell, J. E., and Wheelwright, E. J., *J. Am. Chem. Soc.*, **76**, 612 (1954).
- (531) Spedding, F. H., Powell, J. E., and Wheelwright, E. J., *J. Am. Chem. Soc.*, **76**, 2557 (1954).
- (532) Spedding, F. H., Powell, J. E., and Wheelwright, E. J., *J. Am. Chem. Soc.*, **78**, 34 (1956).
- (533) Spitsyn, V. I., and Voitekh, O., *Dokl. Akad. Nauk SSSR*, **133**, 613 (1960).
- (534) Starik, I. E., and Ginzburg, F. L., *Radiokhimiya*, **1**, 435 (1959).
- (535) Stary, J., *Zh. Neorgan. Khim.*, **4**, 2412 (1959).
- (536) Stary, J., *Collection Czech. Chem. Commun.*, **25**, 86 (1960).
- (537) Stary, J., and Rudenko, N. P., *Zh. Neorgan. Khim.*, **4**, 2405 (1959).
- (538) Staveley, L. A. K., and Randall, T., *Discussions Faraday Soc.*, **26**, 157 (1958).
- (539) Stepanov, A. V., and Shvedov, V. P., *Radiokhimiya*, **1**, 668 (1959).
- (540) Stërba-Böhm, J., *Z. Elektrochem.*, **20**, 289 (1914).
- (541) Stërba-Böhm, J., *Bull. soc. chim. France*, **27**, 185 (1920).
- (542) Stërba-Böhm, J., and Melichar, M., *Collection Czech. Chem. Commun.*, **7**, 131 (1935).
- (543) Stërba-Böhm, J., and Škramovský, S., *Collection Czech. Chem. Commun.*, **1**, 1 (1929).
- (544) Stevens, H. M., *Anal. Chim. Acta*, **20**, 389 (1959).
- (545) Stevenson, P. C., and Nervik, W. E., U. S. Atomic Energy Commission Report NAS-NS-3020 (1961).
- (546) Stewart, D. C., *J. Inorg. Nucl. Chem.*, **4**, 131 (1957).
- (547) Stewart, D. C., Studier, H. M., Mech, J. F., Gindler, J. E., Fields, P. R., Friedman, A. M., Diamond, H., Petheram, M. M., Sjoblum, R. K., and Barnes, R. F., *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, **7**, 321 (1956).
- (548) Stover, B. J., Conway, J. G., and Cunningham, B. B., *J. Am. Chem. Soc.*, **73**, 491 (1951).
- (549) Street, K., and Seaborg, G. T., *J. Am. Chem. Soc.*, **72**, 2790 (1950).
- (550) Strelow, F. W. E., *Anal. Chem.*, **31**, 1201 (1959).
- (551) Subbaraman, P. R., Rajan, K. S., and Gupka, J., *Z. anorg. allgem. Chem.*, **301**, 261 (1959).
- (552) Subbaraman, P. R., Rajan, K. S., and Gupka, J., *Z. anorg. allgem. Chem.*, **304**, 191 (1960).
- (553) Sudarikov, B. N., Zaitsev, V. A., and Puchkov, Yu. G., *Nauchn. Dokl. Vyssheĭ Shkoly, Khim. i Khim. Tekhnol.*, No. 1, 80 (1959); *Chem. Abstr.*, **53**, 13,738h (1959).
- (554) Sures, J. P., Jr., and Choppin, G. R., *J. Inorg. Nucl. Chem.*, **4**, 62 (1957).
- (555) Sutcliffe, L. H., and Weber, J. R., *Trans. Faraday Soc.*, **52**, 1226 (1956).
- (556) Suzuki, N., and Kato, T., *Nippon Kagaku Zasshi*, **80**, 1148 (1959); *Chem. Abstr.*, **54**, 4113a (1960).
- (557) Suzuki, N., and Oki, S., *Bull. Chem. Soc. Japan*, **35**, 233 (1962).
- (558) Suzuki, N., and Oki, S., *Bull. Chem. Soc. Japan*, **35**, 237 (1962).
- (559) Tada, K., Oi, N., and Tsuge, Y., *Nippon Kagaku Zasshi*, **81**, 1554 (1960); *Chem. Abstr.*, **56**, 6637 (1962).
- (560) Takashima, Y., *Nippon Kagaku Zasshi*, **79**, 243 (1958); *Chem. Abstr.*, **52**, 19,689i (1958).

- (561) Tananaev, I. V., and Orlovskii, V. P., *Zh. Neorgan. Khim.*, **7**, 2022 (1962).
- (562) Tananaev, I. V., and Shevchenko, G. V., *Zh. Neorgan. Khim.*, **6**, 1909 (1961).
- (563) Tarayan, V. M., and Eliazyan, L. A., *Izv. Akad. Nauk Arm. SSR, Khim. Nauk*, **13**, 245 (1960); *Chem. Abstr.*, **55**, 10,206i (1961).
- (564) Templeton, D. H., and Dauben, C. H., *J. Am. Chem. Soc.*, **75**, 4560 (1953).
- (565) Terent'eva, E. A., *Usp. Khim.*, **26**, 1007 (1957).
- (566) Thompson, L. C., Doctoral Dissertation, University of Illinois, 1960.
- (567) Thompson, L. C., *Inorg. Chem.*, **1**, 490 (1962).
- (568) Thompson, L. C., *J. Inorg. Nucl. Chem.*, **24**, 1083 (1962).
- (569) Thompson, L. C., and Loraas, J. A., *Inorg. Chem.*, **2**, 89 (1963).
- (570) Thompson, L. C., and Nichol, J. C., *Inorg. Chem.*, **2**, 222 (1963).
- (571) Thompson, S. G., Cunningham, B. B., and Seaborg, G. T., *J. Am. Chem. Soc.*, **72**, 2798 (1950).
- (572) Thompson, S. G., Morgan, L. O., Jones, R. A., and Perlman, I., "The Transuranium Elements," G. T. Seaborg, J. J. Katz, and W. M. Manning, Ed., McGraw-Hill Book Co., New York, N. Y., 1949, part II, pp. 1339-1362.
- (573) Tikhonova, L. I., *Zh. Neorgan. Khim.*, **7**, 822 (1962).
- (574) Tompa, A. S., Doctoral Dissertation, Fordham University, 1961.
- (575) Tompkins, E. R., and Mayer, S. W., *J. Am. Chem. Soc.*, **69**, 2859 (1947).
- (576) Tong, J. Y. P., and King, E. L., *J. Am. Chem. Soc.*, **76**, 2132 (1954).
- (577) Tonosaki, K., and Otomo, M., *Bull. Chem. Soc. Japan*, **35**, 1683 (1962).
- (578) Topp, N. E., *Chem. Ind. (London)*, 1320 (1956).
- (579) Tsong, Y. J., *J. chim. phys.*, **47**, 805 (1950).
- (580) Turner, J. B., Philip, R. H., and Day, R. A., Jr., *Anal. Chim. Acta*, **26**, 94 (1962).
- (581) Ulrich, W. F., Doctoral Dissertation, University of Illinois, 1952.
- (582) Umland, F., and Puckelt, H., *Anal. Chim. Acta*, **16**, 334 (1957).
- (583) Urbain, G., and Sarkar, P. B., *Compt. rend.*, **185**, 593 (1927).
- (584) Van Tassel, J. H., and Wendlandt, W. W., *J. Am. Chem. Soc.*, **82**, 4821 (1960).
- (585) Van Tassel, J. H., Wendlandt, W. W., and Sturm, E., *J. Am. Chem. Soc.*, **83**, 810 (1961).
- (586) van Vleck, J. H., and Frank, A., *Phys. Rev.*, **34**, 1449 (1929).
- (587) van Vleck, J. H., and Frank, A., *Phys. Rev.*, **34**, 1625 (1929).
- (588) Vepňek-Šiška, J., Pliška, V., and Šmirous, F., *Collection Czech. Chem. Commun.*, **24**, 3548 (1959).
- (589) Vetejska, K., *Collection Czech. Chem. Commun.*, **25**, 1895 (1960).
- (590) Vicentini, G., Valarelli, J. V., Perrier, M., and Giesbrecht, E., *J. Inorg. Nucl. Chem.*, **24**, 1351 (1962).
- (591) Vickery, R. C., *J. Chem. Soc.*, 2058 (1950).
- (592) Vickery, R. C., *J. Chem. Soc.*, 1817 (1951).
- (593) Vickery, R. C., *J. Chem. Soc.*, 421 (1952).
- (594) Vickery, R. C., *J. Chem. Soc.*, 4357 (1952).
- (595) Vickery, R. C., *J. Chem. Soc.*, 385 (1954).
- (596) Vickery, R. C., *J. Chem. Soc.*, 255 (1955).
- (597) Vickery, R. C., *J. Chem. Soc.*, 2360 (1955).
- (598) Vickery, R. C., *J. Chem. Soc.*, 3113 (1956).
- (599) Vickery, R. C., *Nature*, **179**, 626 (1957).
- (600) Vickery, R. C., *J. Mol. Spectry.*, **2**, 327 (1958).
- (601) Vickery, R. C., and Sedlacek, R., *Nature*, **181**, 39 (1958).
- (602) Voitekh, O., and Spitsyn, V. I., *Dokl. Akad. Nauk SSSR*, **136**, 339 (1961).
- (603) Wagner, W., *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **23**, 155 (1962).
- (604) Wald, M., *Monatsh.*, **92**, 605 (1961).
- (605) Ward, M., and Welch, G. A., *J. Inorg. Nucl. Chem.*, **2**, 395 (1956).
- (606) Warren, C. G., *J. Inorg. Nucl. Chem.*, **23**, 103 (1961).
- (607) Warren, C. G., and Suttle, J. F., *J. Inorg. Nucl. Chem.*, **12**, 336 (1960).
- (608) Weaver, B., *Anal. Chem.*, **26**, 476 (1954).
- (609) Weidmann, G., and Liebold, G., *Angew. Chem.*, **69**, 753 (1957).
- (610) Weiser, H. B., and Milligan, W. O., *J. Phys. Chem.*, **42**, 669 (1938).
- (611) Weiser, H. B., and Milligan, W. O., *J. Phys. Chem.*, **42**, 673 (1938).
- (612) Wendlandt, W. W., *Science*, **122**, 197 (1955).
- (613) Wendlandt, W. W., *Anal. Chem.*, **27**, 1277 (1955).
- (614) Wendlandt, W. W., *Anal. Chem.*, **28**, 499 (1956).
- (615) Wendlandt, W. W., *Anal. Chim. Acta*, **15**, 533 (1956).
- (616) Wendlandt, W. W., *Anal. Chim. Acta*, **17**, 274 (1957).
- (617) Wendlandt, W. W., and Horton, G. R., *Anal. Chem.*, **34**, 1098 (1962).
- (618) Wenger, P., Duckert, R., and Rusconi, Y., *Helv. Chim. Acta*, **28**, 274 (1945).
- (619) Wenger, P., Duckert, R., and Rusconi, Y., *Helv. Chim. Acta*, **28**, 872 (1945).
- (620) West, R., and Riley, R., *J. Inorg. Nucl. Chem.*, **5**, 295 (1958).
- (620a) Whan, R. E., and Crosby, G. A., *J. Mol. Spectry.*, **8**, 315 (1962).
- (621) Wheelwright, E. J., and Spedding, F. H., *J. Am. Chem. Soc.*, **75**, 2529 (1953).
- (622) Wheelwright, E. J., Spedding, F. H., and Schwarzenbach, G., *J. Am. Chem. Soc.*, **75**, 4196 (1953).
- (623) White, J. A., Williams, H. J., and Sherwood, R. C., *Phys. Rev.*, **128**, 581 (1962).
- (624) Wilkins, D. H., and Smith, G. E., *Talanta*, **8**, 138 (1961).
- (625) Wilkinson, G., and Birmingham, J. M., *J. Am. Chem. Soc.*, **76**, 6210 (1954).
- (626) Wish, L., Freiling, E. C., and Bunney, L. R., *J. Am. Chem. Soc.*, **76**, 3444 (1954).
- (627) Wolf, L., and Bärnighausen, H., *Acta Cryst.*, **13**, 778 (1960).
- (628) Wolf, L., and Massone, J., *J. prakt. Chem.*, [4] **3**, 178 (1956).
- (629) Wolf, L., and Massone, J., *J. prakt. Chem.*, [4] **5**, 14 (1957).
- (630) Wolf, L., and Massone, J., *J. prakt. Chem.*, [4] **5**, 21 (1957).
- (631) Wolf, L., and Massone, J., *J. prakt. Chem.*, [4] **5**, 288 (1957).
- (632) Wolf, L., and Massone, J., *Chem. Tech.*, **10**, 290 (1958).
- (633) Wolfsburg, K., *Anal. Chem.*, **34**, 518 (1962).
- (634) Wong, P., *Hong Kong Baptist Coll. J.*, **1** (1), 85 (1962); *Chem. Abstr.*, **58**, 6433b (1963).
- (635) Wu, C.-K., and Hsü, K.-H., *K'o Hsueh T'ung Pao*, 330 (1959); *Chem. Abstr.*, **54**, 4117i (1960).
- (636) Wünsch, L., *Chem. Listy*, **49**, 843 (1955).
- (637) Wünsch, L., *Collection Czech. Chem. Commun.*, **20**, 1107 (1955).
- (638) Wünsch, L., *Collection Czech. Chem. Commun.*, **26**, 1886 (1961).
- (639) Yakovlev, G. N., Gorbenko-Germanov, D. S., Zenkova,

- R. A., Razbitnoi, N. M., and Kazanskii, K. S., *Zh. Obshch. Khim.*, **28**, 2624 (1958).
- (640) Yakolev, G. N., Kosyakov, V. N., Gorbenko-Germanov, D. S., Zenkova, R. A., Korovin, A. P., and Sobolev, Y. P., *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, **7**, 363 (1956).
- (641) Yang, J. T., and Haïssinsky, M., *Bull. soc. chim. France*, **546** (1949).
- (642) Yatsmirskii, K. B., and Prik, G. A., *Zh. Neorgan. Khim.*, **7**, 62 (1962).
- (643) Yatsmirskii, K. B., and Zhukov, Yu. A., *Zh. Neorgan. Khim.*, **7**, 2807 (1962).
- (644) Yoshida, H., *J. Inorg. Nucl. Chem.*, **24**, 1257 (1962).
- (645) Yoshimura, J., Takashima, Y., and Waki, H., *Nippon Kagaku Zasshi*, **79**, 1169 (1958); *Chem. Abstr.*, **53**, 5015g (1959).
- (646) Yost, D. M., Russell, H., Jr., and Garner, C. S. "The Rare-Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, N. Y., 1947, Chapters 2 and 3.
- (647) Young, J. P., and White, J. C., *Anal. Chem.*, **32**, 1658 (1960).
- (648) Zaborenko, K. B., Zaval'skaya, A. V., and Formin, V. V., *Radiokhimiya*, **1**, 387 (1959).
- (649) Zachariasen, W. H., *J. Am. Chem. Soc.*, **70**, 2147 (1948).
- (650) Zachariasen, W. H., "The Actinide Elements," G. T. Seaborg and J. J. Katz, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1954, Chapter 18.
- (651) Zhuk, N. P., *Zh. Fiz. Khim.*, **28**, 1523 (1954).