Review

Complexation and Separation of Lanthanides(III) and Actinides(III) by Heterocyclic N-Donors in Solutions

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1. Introduction

Lanthanides(III) and actinides(III) belong to hard elements, preferably bound in complexation reactions to the hard oxygen donor atoms. Correspondingly, studies of complexation of these elements in solutions were until the 1980s performed with complexants bonding the complexed metal ion either exclusively to oxygen atoms or to both oxygen and nitrogen atoms. Such complexes may be very stable in solution, but high stability is not the only property desired. Complexation is a very useful tool for separation of metal ions, if utilized in systems involving two immiscible phases. In such cases, the selectivity of the complexation is a characteristic as valuable or still more valuable.

Of two-phase systems, solvent extraction and ion exchange play the most important roles as modern separation methods. This review is concentrated on complexing in solvent extraction, that is, it deals preferably with lipophilic complexants applicable as extractants. Solvent extraction is a highly versatile method, applicable in procedures ranging from laboratory separations to large scale operations. It plays a role in hydrometallurgy, where nuclear technology represents the crucial field. One of the topics attracting attention in recent decades is removal of long-lived, highly toxic isotopes of minor actinides (mainly americium and curium) from high-level radioactive waste (waste partitioning). This operation, accomplished by transmution of the actinides to short-lived isotopes, is a potential way of reducing risks connected with the final waste disposal. The actinides can be removed in a partitioning process consisting of several steps, mostly performed by solvent extraction. One of the steps is separation of the actinides(III) (henceforth An(III)),

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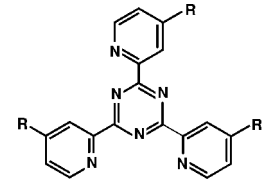
Zdenek Kolarik, born 1933, received his degree of doctor from the University of Brno, then Czechoslovakia. There he performed student research work in the field of analytical chemistry and complex formation, but his subsequent research career was predominantly devoted to nuclear chemistry. In 1957, he joined Nuclear Research Institute in Řež near Prague, where he investigated the separation chemistry of fission products with emphasis on solvent extraction and sorption on hydroxide precipitates. In 1969, he joined Nuclear Research Center (NRI, Kernforschungszentrum) at Karlsruhe, then Federal Republic of Germany. There he was involved in the development of advancements in solvent extraction process for the reprocessing of spent nuclear fuel (Purex process). In 1986−1987, he worked as visiting scientist at Argonne National Laboratory, Argonne, IL, where he studied solvent extraction chemistry of actinides. From 1987, he continued his work at NRI, and in 1990s, he concentrated his effort on development work concerning the separation of minor actinides from high-level liquid radioactive waste. He retired in 1998.

representing a small mass, from a much larger mass of fission product lanthanides(III) (henceforth Ln(III)). Due to very similar chemical properties, the separation of the groups required the identification of complexing agents, preferentially lipophilic, exhibiting the respective selectivity. Clearly preferred are extractants that extract An(III) selectively with respect to Ln(III), and less appreciated are hydrophilic agents that complex the metal ions in aqueous solutions only.

The desired selectivity is not exhibited by the majority of oxygen or oxygen/nitrogen donor extractants. They may be appreciably selective within the Ln(III) or the An(III) series, discriminating well between some adjacent elements, but not between the two groups. This was shown, for example, for thenoyltrofluoroacetone and bis(2-ethylhexyl)phosphoric acid.[1] No noticeable ability to discriminate between Eu(III) and Am(III) is exhibited by hydroxylamine and tropolone derivatives, as well as hydroxynaphthoic acids, and some selectivity for Am(III) is implied for 5,7-dichloro-8-hydroxyquinoline.[2] Diethylenetriaminepentaacetic acid is one An(III)-selective oxygen/nitrogen donor, but it forms complexes only in the aqueous phase.[3]

Desired selectivity for An(III) has neither been achieved in constructing multidentate O-donors with sophisticated preorganized molecules, described in a recent review.[4] The molecules, based on calixarenes, cavitands, trityls, and tripodands, are very efficient extractants for Am(III). However, they seldom extract Am(III) over Eu(III) with a separation factor of >3.

Much more promising are soft nitrogen and sulfur donors. It was shown in the early 1980s that 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ),



R	
H	TPTZ
tert-butyl	2,4,6-tris(4-*tert*-butylpyrid-2-yl)-1,3,5-triazine

a ligand bonding complexed metal ions through soft nitrogen atoms, extracted Am(III) selectively with regard to Eu(III) when the complexes were made extractable by neutralizing their positive charge by lipophilic anions, such as 2-bromodecanoate or dinonylnaphthalenesulfonate.[5,6] It was further shown therein that also bis(2-ethylhexyl)dithiophosphoric acid preferably extracted Am(III) over Eu(III). However, N-donors are preferred in a nuclear application because they consist only of C, H, O, and N atoms and can be incinerated to gaseous products, which after purification can be released into the atmosphere. In contrast, incineration of phosphorus-containing S-donors leaves solid residue, which not only undesirably contributes to the production of radioactive waste but also can retain not easily recoverable residues of actinides.

As the development of partitioning processes has attracted increased attention in the last two decades, the investigations of lanthanide(III) and actinide(III) complexing by N-donors has become more intensive. The work has been concentrated on lipophilic compounds, which could be used as extractants. N-Donors turned out to be really promising reagents for the Ln(III)/An(III) separation, when compounds with noticeable selectivity for An(III) were recently found. 2,6-Bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines[7,8] can be mentioned as an example of ligands that are much more selective than TPTZ and also able to extract lanthanides(III) selectively with regard to Y(III).[9]

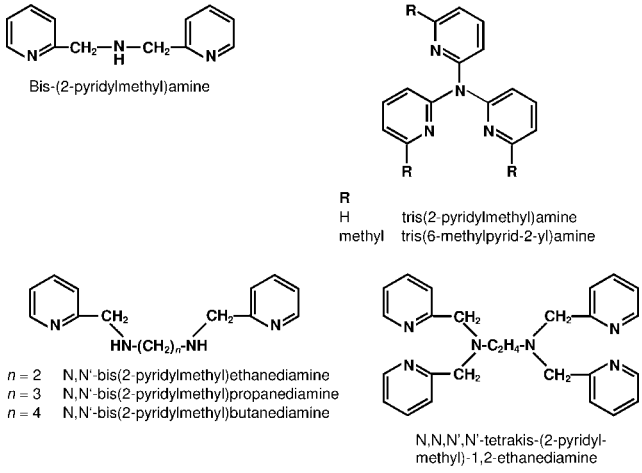
A considerable part of the work on An(III)-selective N-donors has been done in Europe. Especially extensive work was performed in the frame of two research programs financially supported by the European Commission, namely, NEWPART[10] and PARTNEW.[11] Information on the participants and an overview of results of the work can be found in the two cited sources, which are final reports of the programs. A historical look back at the development of the work has been given recently.[12]

It would be too a narrow scope to review only the search for An(III) selective complexants. It is of interest to survey the complexation of Ln(III) and An(III) in a scope much more extensive than mere observation of selectivities in solvent extraction equilibria. The use of soft N-donors for the complexation of hard ions (e.g., see ref 13) might disclose selectivities applicable also to other separations than that of An(III) from Ln(III). Emphasis is laid on at least tridentate N-donors, while bipy and phen will be dealt with only marginally.

This review covers the time span from the early 1980s to the end of 2007. As far as possible, it presents numerical

data, which are preferentially presented in capacious tables and subsequently discussed in the text. To facilitate the alternate orientation in the tables and the text, rows in the tables are numbered and pointers to the rows are given as italic numerals in curly brackets. The pointers are related to a table by the table number given as superscript behind the closing bracket. The configuration of most complexants dealt with in the review is shown graphically (see structural formulas **1**).

2. Properties of N-Donors in Solutions



Structural formulas **1**

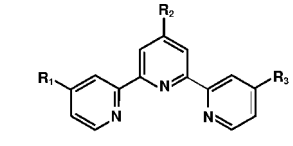
2.1. Basicity

Basicity of N-donors is an important property, because it determines the extent to which the H^+ ions compete with the Ln^{3+} or An^{3+} ions for the N-donor ligand. Since a separation procedure is urgently needed in which An(III) are extracted from acidic medium (such as >0.1 M HNO_3), weakly basic N-donor extractants are preferable.

2.1.1. Data on the Protonation of Selected N-Donors

Protonation constants are gathered in Table 1. Thorough critical evaluation of the constants is possible in few cases only. Thus, the constants are only categorized as thermodynamic, concentration, and mixed or unspecified constants. Since the experimental work is often unsatisfactorily described in the original sources, most constants belong to the last type. Especially frequent is lack of detailed information on the type of electrodes. It is a common practice that a scale is used for H^+ ions, which (according to a IUPAC convenience) is accepted as activity, while a molarity scale is applied to other interacting components of the system.

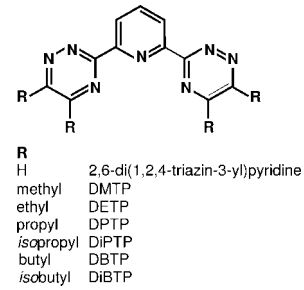
It has been considered in one case only that various conformation forms of protonated terpy



R_1	R_2	R_3	
H	H	H	terpy
tert-butyl	*tert*-butyl	*tert*-butyl	tri-*tert*-butylterpy
H	alky*/aryl**	H	4'-(alkyl/aryl)terpy
H	-PO_3(OH)	H	4'-phosphonatoterpy

*alkyl = methyl,octyl, dodecoxyl,3-phenylpropoxyl;
**aryl = phenyl, tolyl, 2,5-dihydroxyphenyl, 2,5-dimethoxyphenyl, and 4-nitrophenyl

can participate in protonation equilibria.[14] [BH^+] in the K_1 value from this source {7}[T1] comprises the sum of the concentrations of symmetric and asymmetric forms, which are in tautomeric equilibrium. Since [BH_2^{2+}] can adopt only a symmetric form, it is assumed to dissociate to an asymmetric form of [BH^+]. Thus, the concentration of symmetric [BH^+] is not comprised in K_2.



R	
H	2,6-di(1,2,4-triazin-3-yl)pyridine
methyl	DMTP
ethyl	DETP
propyl	DPTP
*iso*propyl	DiPTP
butyl	DBTP
*iso*butyl	DiBTP

Not included in Table 1 are protonation constants of hydrazides of the type $(R_1)(R_3)C{=}NNH(R_2)$, where R_1 and R_2 are combinations of 2-pyridyl, 5(6)-methyl-2-pyridyl, 5-chloro-2-pyridyl, 5-nitro-2-pyridyl, 2-quinolyl, and isoquinolyl and R_3 is H or methyl. None of these compounds has been investigated as a complexant for Ln(III) and An(III), even if they could form complexes at pH < 3. Especially low basicity is exhibited by compounds with nitropyridyl as R_1 or R_2, with log $K_1 = 3.6-4.0$ and log $K_2 = -0.4$ to 1.0. The other compounds have log $K_1 = 5.4-6.4$ and log $K_2 = 2.1-3.8$. All of them are fully deprotonated at pH > 10, releasing the imino hydrogen as a H^+ ion. The corresponding log K value is ~11.2 in the compounds bearing a nitro group and 13.7−15.4 in the others.[15−18]

2.2. Protonation in an Organic Solvent

When protonation constants have been determined in a system consisting of two liquid phases, it has been supposed that protonated forms are present predominantly in the aqueous phase and their concentration in the organic phase is negligible in comparison with that of nonprotonated species.[11] However, DPTP is so lipophilic that its protonated forms are partially transferred into the organic phase. If a solution of DPTP in THP/1-octanol (7/3 v/v) is equilibrated with 0.1−4 M HNO_3 and 0 or 2 M NH_4NO_3, DPTP is present in the organic phase as the partially protonated species $B{\cdot}HNO_3$ and $B{\cdot}(HNO_3)_2$. The respective equilibrium constants are $K_{H(1)} = [B{\cdot}HNO_3]_{org}/(H^+)_{aq}(NO_3^-)_{aq}(B)_{aq} = 4$ and $K_{H(2)} = [B{\cdot}(HNO_3)_2]_{org}/(H^+)_{aq}^2(NO_3^-)_{aq}^2(B)_{aq} = 0.4$, with molar concentrations used in the organic phase. Molal activities are applied in the aqueous phase,[19] as obtained by conversion of molal concentrations with the aid of specific interaction theory.[20] If the formulation of the constants is accepted, they reveal that DPTP is protonated in the organic phase to >10% at >0.2 M HNO_3 in the aqueous phase, and the diprotonated form plays a role at >2 M HNO_3 in the aqueous phase. It indeed is true that specific interaction theory has widely been used for the treatment of data obtained at variable ionic strength. Nevetheless, a strictly rigorous consideration might impose the basic objection that it is impossible to determine activities of single ions. Further, the relevance of the constants could be reduced by the fact that they were calculated without regarding self-association of DPTP in the organic phase, which had been described earlier.[8]

Table 1. Protonation Constants of Heterocyclic N-Donors in Aqueous Solutions, if Not Given Otherwise[a]

nr.	compound	medium (*type of constant*)	T, °C	method	log K_1	log K_2	log K_3; log K_4
1	bipy	$I = 0$ (*th*) or 0.01 (*mu*)	25	pot	4.34[b]		
2		variable HCl or H_2SO_4 (*mu*)	25	pot		−0.2[b]	
3		0.2 M $LiNO_3$/50% EtOH	25	pot	3.47[b]		
4		0.2 M $LiNO_3$/50% PrOH	25	pot	3.41[b]		
5		0.2 M $LiNO_3$/50% Me_2CO	25	pot	3.58[b]		
6	terpy	$I = 0.1$, recalcd for $I = 0$ (*th*)	22	sp	4.33(3)[c]	2.64(7)[c]	
7		(H,K,Na)phthalate, $I = 0.01$ (*mu*)	25	sp	4.66(1)[14]		
8		0.001 M (H,Na)Cl (*mu*)	13.2	sp		3.46(5)[14]	
9		0.001 M (H,Na)Cl (*mu*)	25	sp		3.27(5)[14]	
10		0.001 M (H,Na)Cl (*mu*)	36.6	sp		3.08(4)[14]	
11		0.01 M (H,Na)Cl (*mu*)	25	sp		3.28(2)[14]	
12		(H,K,Na)phthalate, $I = 0.01$ (*mu*)	13.2	sp	4.68(3)[14]		
13		(H,K,Na)phthalate, $I = 0.05$ (*mu*)	25	sp	4.81(2)[14]		
14		var. HCl (I not given) (*mu*)	25	sp	4.9[24]	3.4[24]	
15		(H,NH_4)(CH_3COO), $I = 0.1$ (*mu*)	rt	sp	4.71(6)[23]	3.57(4)[23]	
16		0.1 M KCl (*mu*)	35	sp	4.16[35]	2.59[35]	
17		0.2 M KCl (*cc*)	25	pot	4.54(3)[d]	3.57(2)[d]	
18		1 M KCl (*mu*)	25	sp	4.9(3)[10,21]	4.0(2)[10,21]	
19		0.1 M (H,K)NO_3 (*cc*)	25	pot	4.64(1)[34]	3.42(2)[34]	
20		1.0 M (H,Na)NO_3 (*mu*)	25	dis	3.2(2)[11]	2.8(2)[11]	1.8(5)[11]
21		0.1 M K_2SO_4 (*mu*)	rt	pot	4.69[e]	3.99[e]	
22		0.1 M KNO_3/16.5 wt % MeOH	25	pot	4.60[f]	3.16[f]	
23		0.1 M KNO_3/44.2 wt % MeOH	25	pot	3.90[f]	2.70[f]	
24		variable HCl/76 vol % MeOH	25	sp	3.6[24]	2.0[24]	
25		1 M (H,Li)Cl/76 vol % MeOH	25	sp	3.6[21]	2.9[21]	
26		2 M (H,Li)Cl/80 vol % MeOH	25	sp	3.2(2)[10]	2.9(2)[10]	
27		0.1 M KNO_3/16.6 wt % EtOH	25	pot	4.90[f]	2.90[f]	
28		0.1 M KNO_3/44.3 wt % EtOH	25	pot	3.92[f]	2.44[f]	
29		0.1 M KNO_3/16.5 wt % Me_2CO	25	pot	5.10[f]	3.08[f]	
30		0.1 M KNO_3/44.2 wt % Me_2CO	25	pot	3.62[f]	2.62[f]	
31e		0.1 M KNO_3/19.2 wt % DMF	25	pot	5.30[f]	3.98[f]	
32		0.1 M KNO_3/48.8 wt % DMF	25	pot	3.28[f]	2.82[f]	
33		0.1 M KNO_3/21.6 wt % DMSO	25	pot	5.46[f]	3.88[f]	
34		0.1 M KNO_3/52.4 wt % DMSO	25	pot	3.94[f]	2.86[f]	
35		0.2 M $NaClO_4$/50 vol % EtOH	20	pot	4.37[g]	3.17[g]	
36	4′-methylterpy	2 M (H,Li)Cl/80 vol % MeOH	25	sp	3.4(2)[10]	2.9(2)[10]	
37	4′-octylterpy	2 M (H,Li)Cl/80 vol % MeOH	25	sp	3.4(2)[10]	2.8(2)[10]	
38	4′-phosphonatoterpy	0.5 M KNO_3 (*cc*)	25	NMR pot	4.65(1)[25]	3.55(3)[25]	
39	2,2′:6′,2″:6″,2‴-quaterpyridyl	pH 2.0 (*mu*)	21	sp	∼3.2[h]		
40	2,6-di(2-benzimidazolyl) pyridine	var. HCl/76 vol % MeOH	25	sp	4.5[24]	1.8[24]	
41		1 M (H,Li)Cl/80 vol % MeOH	25	sp	4.5[10]	1.8[10]	
42	2,6-bis(1,2,4-triazin-3-yl) pyridine	var. HCl/76 vol % MeOH	25	sp	3.3[24]	1.0[24]	
43	DMTP	var. HCl (*mu*)	25	sp	1.2[24]		
44		var. HCl/76 vol % MeOH	25	sp	1.8[24]	<0[24]	
45	2,6-di(2-pyridyl)pyrimidine	var. HCl/76 vol % MeOH	25	sp	3.2[24]	1.0[24]	
46	2-amino-4,6-di(2-pyridyl)-1, 3,5-triazine	var. HCl/76 vol % MeOH	rt	sp	3.5[24,111]	1.7[24,111]	

Table 1. Continued

nr.	compound	medium (*type of constant*)	*T*, °C	method	log K_1	log K_2	log K_3; log K_4
47	TPTZ	<0.03 M HNO_3 (*cc*)	rt	sol	3.55(7)[33]	2.72(6)[33]	
48		I < 0.005, pH > 2.7 (*mu*)	25	sol	3.6(2)[11]	2.7(2)[11]	
49		var. HCl (*mu*)	25	sp	3.0[24]	0.8[24]	
50		(H,NH_4)(CH_3COO), I = 0.1 (*mu*)	rt	sp	3.4(1)[23]	2.2(2)[23]	
51		0.1 M (H,K)Cl (*mu*)	25	pot	3.10[31]		
52		0.1 M (H,K)Cl (*cc*)	25	sp	3.53[i]	2.73[i]	
53		0.23 M (H,Na)Cl (*cc*)	25	sp	2.82(1)[j]	2.7(3)[j]	
54		1 M (H,K)Cl (*mu*)	rt		3.8(2)[27]	2.7(3)[27]	
55		1 M KCl (*mu*)	25	sp	4.5[21]	1.8[21]	
56		var. HCl/76 vol % MeOH	25	sp	2.9[24]	0.7[24]	
57		1 M (H,Li)Cl/76 vol % MeOH	25	sp	2.3[21]	0.9[21]	
58		1 M (H,Li)Cl/80 vol % MeOH	25	sp	2.9(1)[10]	0.70(5)[10]	
59	di(2-pyridyl)amine	0.1 M KNO_3 (*cc*)	20	pot	7.14[28]		
60		I = 0.5 (NO_3^-) (*cc*)	25		8.74[k]		
61	bis(2-pyridylmethyl)amine	0.1 M KNO_3 (*cc*)	20	pot	7.11(2)[29]	2.48(5)[29]	
62	tris(2-pyridylmethyl)amine	I = 0.1 (*cc*)	20	pot	6.17(2)[l,29]	4.35(3)[l,29]	2.55(3)[l,29]
63	tris[(6-methyl-2-pyridyl)methyl]amine	0.1 M KNO_3 (*cc*)	20	pot	6.94(2)[29]	5.13(2)[29]	3.45(2)[l,29]
64	tris(2-pyrazylmethyl) amine	1 M (H,Li)Cl (*mu*)	22	sp	3.00(5)[89]		
65	*N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine	0.1 M KNO_3 (*cc*)	25	pot	8.16[30]	5.33[30]	
66	*N*,*N*′-bis(2-pyridylmethyl)-1,3-propanediamine	0.1 M KNO_3 (*cc*)	25	pot	8.33[30]	7.40[30]	
67	*N*,*N*′-bis(2-pyridylmethyl)-1,4-butanediamine	0.1 M KNO_3 (*cc*)	25	pot	9.06[30]	7.56[30]	
68	*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethanediamine	0.1 M KNO_3 (*cc*)	20	pot	7.19(2)[l,29]	4.86(2)[l,29]	3.35(3);[l,29] 2.95(3)[l,29]
69		0.1 M $NaNO_3$ (*mu*)	25	pot	7.2[m]	4.8[m]	3.3;[m] 2.6[m]

[a] Determined by potentiometric titration (pot), spectrophotometry (sp), distribution measurements (dis), solubility measurements (sol), and NMR. Type of constant in aqueous solutions: th = thermodynamic, cc = concentration, and mu = mixed or unspecified. Digit in parentheses after a constant denotes the confidence limit of the last decimal place. $K_1 = [BH^+][H^+]^{-1}[B]^{-1}$; $K_2 = [BH_2^{2+}][H^+]^{-1}[BH^+]^{-1}$; $K_3 = [BH_3^{3+}][H^+]^{-1}[BH_2^+]^{-1}$. [b] From McBryde, W. A. E., Ed., A Critical Review of Equilibrium Data for Proton- and Metal Complexes of 1,10-Phenanthroline, 2,2′-Bipyridyl and Related Compounds, IUPAC Chemical Data Series, No. 17.; Pergamon Press: Oxford, U.K., 1978. [c] From Martin R. B.; Lissfelt J. A. J. Am. Chem. Soc. 1956, 78, 938. [d] From Farkas, E.; Enyedi, É. A.; Micera G.; Garribba E. Polyhedron 2000, 19, 1727. [e] From James, B. R.; Williams, R. J. P. J. Chem. Soc. 1961, 2007. [f] From El-Gahami, M. A.; Ibrahim, S. A.; Fouad, D. M.; Hammam, A. M. J. Chem. Eng. Data 2003, 48, 29. [g] From Abdalla, E. M.; Mahmoud, M. R. J. Indian Chem. Soc. 1995, 72, 13. [h] From Bergh, A.; Offenhartz, P. O'D.; George, P.; Haight, G. P., Jr. J. Chem. Soc. 1964, 1533. [i] From Pagenkopf, G. K.; Margerum, D. W. Inorg. Chem. 1968, 7, 2514. [j] From Prasad, J.; Peterson, N. C. Inorg. Chem. 1971, 10, 88. [k] From Martell, E. E.; Smith, R. M. Critical Stability Constants; Plenum Press: New York, 1974, 1975, 1976, 1977, 1982, 1989; Vols. 1−6. [l] From Anderegg, G.; Wenk, F. Helv. Chim. Acta 1967, 50, 2330. [m] From Takeshita, K.; Watanabe, K.; Nakano, Y.; Watanabe, M. Hydrometallurgy 2003, 70, 63.

2.3. Protonation of N-Donors in Aqueous Systems

2.3.1. Terpy and Its Derivatives

Based on data in Table 1, the influence of variables on the protonation constants can be assessed to some extent. Most investigated has been the protonation of terpy. Published data give more or less consistent sets of log K_1 {*6,7,13,15,17−21*}[T1] and, still more log K_2 {*6,9,11,14,15,17−21*}[T1] values indicating their increase with ionic strength up to I = 0.3. However, two very different pairs of the log K_1 and log K_2 values (4.9, 4.0[21] {*18*}[T1] and 3.2, 2.8[11] {*20*}[T1]) have been reported for I = 1. The higher values {*18*}[T1] were determined spectrophotometrically, but their origin and details of their determination are not specified in the original source.[21] The lower values[11] {*20*}[T1] were calculated from the distribution of terpy between *tert*-butylbenzene and 1 M $NaNO_3$ (good fit was obtained in reevaluation by the present author also with a slightly modified set of log K values, see Figure 1). To obtain more information, pH values of HNO_3 solutions contacted with a 0.1 M solution of terpy in *tert*-butylbenzene[21] were evaluated in this review. They do not yield single log K values, but they give the sum log K_1 + log K_2 = 7.9, which lies between log K_1 + log K_2 = 8.9[21] {*18*}[T1] and log K_1 + log K_2 = 6.0[11] {*20*}[T1]. Thus, the sum 7.9 supports neither data but, lying nearer to the sum 8.9,[21] it insinuates that the log K values from ref 11 might be too low.

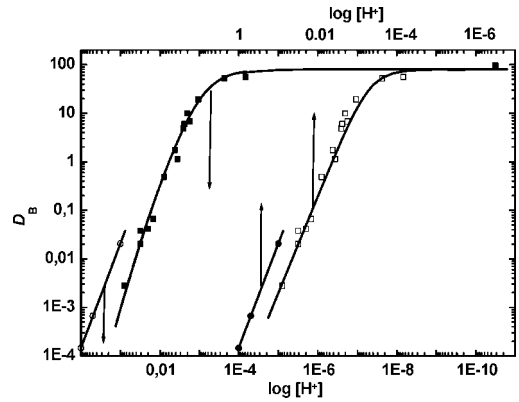


Figure 1. Distribution of terpy between *tert*-butylbenzene and 1 M $NaNO_3$ (□, adapted from ref 11) and between TPH and HNO_3 solutions (line with slope 2.1, ○, adapted from 21). Initially 0.02 M terpy in TPH, room temperature; unspecified initial terpy concentration in *tert*-butylbenzene, 25 °C. Solid squares: Fitting of the data with log K_1 = 3.20, log K_2 = 3.00, log K_3 = 1.64, and log K_d = 1.90. Open squares: Fitting of the same data with from log K_1 = 3.08, log K_2 = 3.52, and log K_d = 1.90.

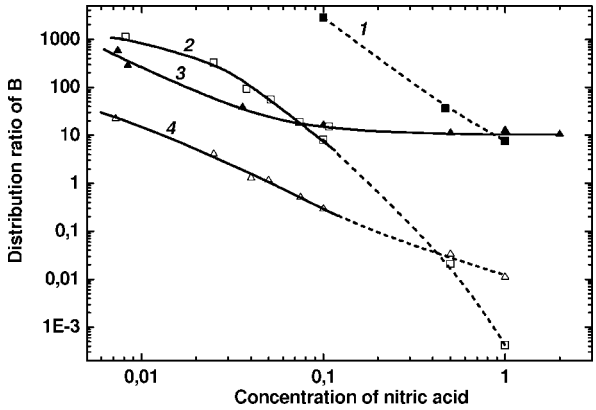


Figure 2. Distribution of 2,4,6-tris(4-*tert*-butylpyrid-2-yl)-1,3,5-triazine (curve 1), TPTZ (curve 2), 4,4′,4″-*tert*-butylterpy (curve 3), and terpy (curve 4) between aqueous solutions of nitric acid and 1 M 2-bromodecanoic acid in TPH. Initially 0.02 M N-donors, room temperature. Adapted by permission of Elsevier (Copyright 1998) from ref 32. Solid-line sections were evaluated by curve fitting to determine protonation constants and partition coefficients.

It cannot be clearly postulated whether terpy is noticeably triprotonated at acid concentrations down to 1 M. The only published log K_3 value (1.8[11] {*20*}^{T1}) was calculated from the dependence of the distribution ratio of terpy on pH with *tert*-butylbenzene as diluent. Figure 1 shows that the steepness of the dependence really indicates the presence of BH_3^{3+} species at pH < 2 (left curve), and there are systematic deviations of experiment from calculation at pH 2−3 if no triprotonated species is assumed to be formed (right curve). This makes the triprotonization plausible. Contrary to results with *tert*-butylbenzene diluent, the log D_B vs log [H^+] dependence with the TPH diluent is a straight line with a slope of 2.1 at 0.075−1.0 M HNO_3 (Figure 1). This in turn indicates only weak triprotonation of terpy in this acidity region.

Terpy is clearly not triprotonated in the aqueous phase if 2-bromodecanoic acid is present in the organic phase. Curve fitting made by the present author reveals that the distribution of terpy between 1 M 2-bromodecanoic acid in TPH and 0.007−0.1 M nitric acid (Figure 2, solid part of curve 4) is controlled by stepwise formation of a diprotonated cation. The fitting yields log $K_1 = 3.84 \pm 0.05$ and log $K_2 = 1.94 \pm 0.05$, that is, indeed lower values than those given in Table 1 for log K_1 {*6,7,13,15,17−19,21*}^{T1} and for log K_2 {*6,9,11,14,15,17−21*}^{T1}. The discrepancy could be explained by an influence of α-bromodecanoic acid, which is able to form hydrogen-bonded complexes with terpy.

As further seen in Figure 2, the log D_B vs pH dependence of terpy (curve 4) and still more 4,4′,4″-tri-*tert*-butylterpy (curve 3) tend to level off at >0.1 M HNO_3. This phenomenon is explained in the original paper[32] by attaining a degree of protonation that is not further enhanced at increasing HNO_3 concentration. However, it is assumed that the N-donor is protonated predominantly in the aqueous phase, and then at constant protonation the log D_B vs pH dependence would have to be a straight line with an integral negative slope. Independence of the distribution ratio of the HNO_3 concentration shows that the degree of protonation of the N-donor is the same in both phases. It is quite plausible that protonated species can exist in the organic phase as hydrogen-bonded complexes with 2-bromodecanoic acid. Complexing of the N-donors also in the aqueous phase is possible, even if the concentration of a monomeric form of the acid in the aqueous phase can be estimated[22] as formally much lower ($\sim 6 \times 10^{-5}$ M) than that of the N-donors. This indeed would be true if the acid interacts only with water and can be regarded as "free". Interaction with an H acceptor could accommodate much larger amounts of the acid in a bound form.

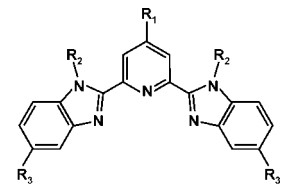
The log K_2 value of terpy decreases from 3.46 to 3.08[14] with increasing temperature at 13.2 to 36.6 °C {*8−10*}^{T1}, and the plot ln K_2 vs $1/T$ is strictly linear. Both K_1 and K_2 are higher at room temperature (4.71, 4.16[23]) {*15*}^{T1} than at 35 °C (3.57, 2.59[35]) {*16*}^{T1}.

The log K_1 and log K_2 values of terpy in the presence of 16−22% organic solvents are similar to those in water or higher. Log K_1 increases in the order of additives MeOH (4.60) {*22*}^{T1} < EtOH (4.90) {*27*}^{T1} < Me_2CO (5.10) {*29*}^{T1} < DMF (5.30) {*31*}^{T1} < DMSO (5.46) {*33*}^{T1} and log K_2 in the order EtOH (2.90) {*27*}^{T1} < Me_2CO (3.08) {*29*}^{T1} < MeOH (3.16) {*22*}^{T1} < DMSO (3.88) {*33*}^{T1} < DMF (3.98) {*31*}^{T1}. Enhancement of the solvent fraction to 44−52% suppresses the K_1 by a factor of 5−100 and the K_2 by a factor of 3−15. Then log K_1 increases in a quite different order than at the lower fraction of the organic solvent, namely, DMF (3.28) {*32*}^{T1} < Me_2CO (3.62) {*30*}^{T1} < MeOH (3.90) {*23*}^{T1} ≈ EtOH (3.92) {*28*}^{T1} ≈ DMSO (3.94) {*34*}^{T1}. However, K_2 increases in a similar order as at the lower organic fraction, namely, EtOH (2.44) {*28*}^{T1} < Me_2CO (2.62) {*30*}^{T1} < MeOH (2.70) {*23*}^{T1} < DMF (2.82) {*32*}^{T1} < DMSO (2.86) {*34*}^{T1}.

K_1 and K_2 of terpy in 76 vol % MeOH (3.6, 2.0) {*24*}^{T1} are lower than those in water (4.9, 3.4) {*14*}^{T1}, by a factor of 20 and 25, respectively. A more detailed investigation of the effect of methanol shows that the decrease of the logarithms of both values with increasing volume fraction of MeOH is fairly linear.[24]

To compare, the log K_1 value of bipy is suppressed by adding MeOH, EtOH, and Me_2CO to a concentration of 50%, but it is little influenced by the nature of the solvent {*1,3−5*}^{T1}.

Introduction of methyl {*36*}^{T1}, octyl {*37*}^{T1},[10] and phosphonate[25] group {*38*}^{T1} at the 4′-position of terpy has no visible effect on the log K_1 value (3.4−3.55). The phosphonate group of 4-phosphonatoterpy is monoionized when the N atoms of the lateral pyridine rings are stepwise deprotonated.[25] 2,6-Bis[1-(1-*S*-neopentyl)benzimidazol-2-yl]pyridine



R_1	R_2	R_3	
H	H	H	2,6-di(2-benzimidazolyl)pyridine
H	alkyl*	H	2,6-bis(1-alkylbenzmidazol-2-yl)pyridine
phenyl	3,5-dimethoxybenzyl	H	4-(4-phenyl)-2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine
4-nitrophenyl	3,5-dimethoxybenzyl	H	4-(4-nitrophenyl)-2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine
4-dimethylaminophenyl	3,5-dimethoxybenzyl	H	4-(4-dimethylaminophenyl)-2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine
carboxyl	methyl	H	4-carboxy-2,6-bis(1-mehylbenzimidazol-2-yl)pyridine
Dodecoxyl	H	H	4-dodecoxy-2,6-di(2-benzimidazolyl)pyridine
H	ethyl	methyl	

*alkyl = methyl, ethyl, propyl, hexyl, octyl, 1-S-neopentyl, and 3,5-dimethoxybenzyl

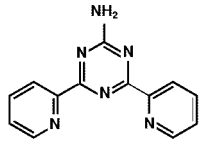
is indicated by electrospray mass spectrometry to form in MeCN at room temperature not only the common monoprotonated species BH^+ but also a demiprotonated species B_2H^+.[26]

2.3.2. TPTZ and DMTP

The log K_1 and log K_2 values of TPTZ {47−55}[T1] can hardly be characterized as functions of ionic strength at $I <$ 0.005 to 1.0, mainly due to the disagreement of values at I = 1 (3.8 ± 0.2 and 2.7 ± 0.3[27] {54}[T1], and 4.5 ± ≥0.1 and 1.8 ± ≥0.1[21] {55}[T1]) reported in different sources. The log K_1 and log K_2 values at variable HCl are similar in water (3.0, 0.8) {49}[T1] and 76% MeOH (2.9, 0.7[24]) {56}[T1], but at I = 1 they are generally higher in water[21,27] {54,55}[T1] than in 76% MeOH (2.3, 0.9[21] {57}[T1], 2.9, 0.7[10] {58}[T1]).

To some surprise, curve fitting (present author) reveals that the distribution of TPTZ between 1 M 2-bromodecanoic acid in TPH and 0.007−0.1 M nitric acid (Figure 2, solid part of curve 2) is controlled by the formation of a triprotonated species in one single step, that is, without intermediate formation of mono- and diprotonated species. The logarithm of the protonation constant $\beta_3 = [BH_3^{3+}][B]^{-1}[H^+]^{-3}$ is 5.2 ± 0.1. As with terpy, the value from the curve fitting is unexpectedly low in comparison with most published values of log K_1 + log K_2 {47,48,50,52,53−55}[T1]. Only one source {49}[T1] reports a lower sum. The one-step triprotonation can be explained by influence of 2-bromodecanoic acid.

The K_1 and K_2 of 2-amino-4,6-di(2-pyridyl)-1,3,5-triazine



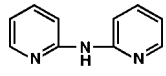
2-amino-4,6-di(2-pyridyl)-1,3,5-triazine

at 76 vol % MeOH are lower than those at 30 vol % MeOH, by a factor of 2 and 10, respectively. The decrease of the logarithms of the constants with increasing volume fraction of MeOH is linear.[24]

DMTP is less basic than any other purely heterocyclic N-donor. Its log K_1 value increases linearly with volume fraction of methanol, being 1.8 in 76 vol % MeOH {44}[T1] and 1.2 in water[24] {43}[T1].

2.3.3. Pyridyl-Substituted Alkaneamines

N-Donors derived from aliphatic amines {59−69}[T1] are in general more strongly basic than heterocyclic N-donors {1−58}[T1]. This is observed in disubstituted {59−61}[T1] and trisubstituted {62−64}[T1] amines, disubstituted alkanediamines {65−67}[T1], and a tetrasubstituted ethanediamine {68,69}[T1]. Introduction of a methylene group between a 2-pyridyl substituent and an amine N atom plays apparently no role, because di(2-pyridyl)amine {59}[T1]



Di-2-pyridylamine

has practically the same log K_1 value (7.14[28]) as bis(2-pyridylmethyl)amine (7.11[29]) {61}[T1]. The latter, and probably also the former, is protonated at the aliphatic N-atom. The lower basicity of this N-atom in comparison with aliphatic secondary amines is ascribed to an effect of the 2-pyridylmethyl substituents. The effect is so strong that tris(2-pyridylmethyl)amines and *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethanediamine are protonated preferentially at pyridyl N-atoms.[29] A role is played by methyl substitution at the pyridyl ring: all three log K values of tris[(6-methyl-2-pyridyl)methyl]amine (6.94, 5.13, 3.45) {63}[T1] are higher than those of tris(2-pyridylmethyl)amine (6.17, 4.35, 2.55) {62}[T1]. Both the log K_1 and log K_2 values of *N*,*N*′-bis(2-pyridylmethyl)-1,*i*-alkanediamine increase in the alkane order ethane (i = 2; 8.16, 5.33[30]) {65}[T1] < propane (i = 3; 8.33, 7.44[30]) {66}[T1] < butane (i = 4; 9.06, 7.56[30]) {67}[T1]. The log K_1 and log K_2 values of *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethanediamine (7.19, 4.86[29]) {68}[T1] are lower than those of *N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine (8.16, 5.33[30]) {65}[T1].

2.4. Solubility and Distribution between Two Liquid Phases

In unprotonated form the complexants are slightly soluble in water, and they become more soluble with increasing concentration of H^+ ions, that is, with increasing degree of protonation. The solubility of terpy and TPTZ in water without pH adjustment is 5 × 10^{-4} M and 2 × 10^{-5} M, respectively, and it is as high as >0.5 M in 1 M HNO_3.[21] The solubility of TPTZ in an acetate-buffered aqueous solution at pH 4.5 is 9.2 × 10^{-5} M.[31]

The ligands are little soluble in the aliphatic TPH solvent, where a concentration as low as 0.06 M terpy can be attained. The solubility of TPTZ in TPH is contradictorily given as 2 × 10^{-4} M[32] and 10^{-5} M.[21] However, the solubility is enhanced by introducing lipophilic substituents into the structure. Then the solubilities in TPH are 0.5 M 4′-octylterpy, 0.02 M 4,4′,4″-tri-*tert*-butylterpy, and 0.002 M 2,4,6-tris(4-*tert*-butylpyrid-2-yl)-1,3,5-triazine. Notice that one *n*-octyl group enhances the solubility more than three *tert*-butyl groups in a molecule. Practicable concentrations are attained in the presence of 1 M α-bromodecanoic acid, namely, >0.5 M terpy, >0.7 M 4′-octylterpy, >0.3 M 4,4′,4″-tri-*tert*-butylterpy, >0.1 M TPTZ, and 0.05 M 2,4,6-tris(4-*tert*-butylpyrid-2-yl)-1,3,5-triazine.[32]

Important is the knowledge of the distribution coefficient of N-donors between an organic and an aqueous phase in dependence on pH, such as shown in Figures 1 and 2. They illustrate possible losses of N-donor extractants to the aqueous phase in solvent extraction separation procedures, where it is always attempted to keep the extractant as completely as possible in one single organic stream. If the distribution ratio of the extractant is not high enough, a fraction of it is lost either to a waste stream with which it is eventually discarded or to a product stream from which it must be removed.

The partition coefficient of unprotonated terpy between *tert*-butylbenzene and 1 M $(Na,H)NO_3$ has been given as 360 ± 5 (pH measurement in the two-phase system)[21] but, unfortunately, for an unspecified concentration of α-bromodecanoic acid (supposedly 1 M). Reevaluation of the pH dependence of the distribution ratio of terpy between 1 M $NaNO_3$ and *tert*-butylbenzene (Figure 1) yields 80 in the absence of 2-bromodecanoic acid. If 1 M 2-bromodecanoic acid is present, the K_d of unprotonated terpy and TPTZ

between TPH and very diluted HNO_3 is 2000 ± 200 and 1100 ± 100, respectively (curve fitting, curves 2 and 4 in Figure 2).

The effect of substituents at the pyridyl rings on the lipophilicity of N-donors is shown in Figure 2. So 4,4′,4″-tri-*tert*-butyl terpy (curve 3) is more lipophilic than terpy (curve 4), and 2,4,6-tris(4-*tert*-butylpyrid-2-yl)-1,3,5-triazine (curve 1) is more lipophilic than TPTZ (curve 2).

2.5. Self-Association

The phenomenon was taken into consideration in order to improve the slope analysis of data on solvent extraction of Am(III) and Eu(III) by 2,6-bis(5,6-propyl-1,2,4-triazin-3-yl)pyridines. It turned out that DPTP and DiPTP really formed dimers and trimers at 0.001−0.04 M combined concentration in a solution of TPH/2-ethyl-1-hexanol (4/1 v/v), which was in equilibrium with 1.90 M $(H,NH_4)NO_3$. The distribution of the complexants between the phases is described by the partition coefficient $K_d = [B]_{org}/[B]_{aq}$ and the oligomerization constants $K_2 = [B_2]_{org}/[B]_{org}^2$ and $K_3 = [B_3]_{org}/[B]_{org}^3$. The constants are conditional values, because H^+ ions participate in the partition and self-association equilibria. For DPTP, the constants are $K_d = 72.3$, $K_2 = 8.1$, and $K_3 = 146$ at 0.30 M HNO_3 and $K_d = 14.0$, $K_2 = 12.2$, and $K_3 = 580$ at 0.90 M HNO_3. DiPTP oligomerizes much less intensely, the constants being $K_d = 65$, $K_2 = 2.4$, and $K_3 \approx 5$ at 0.30 M HNO_3. When 0.04 M DPTP in TPH/2-ethyl-1-hexanol is in equilibrium with aqueous 0.28−0.87 M HNO_3, the ratio $[HNO_3]_{org}/[DPTP]_{total,org}$ is 0.4 to 0.8_5. Analysis of the data implies that monomeric DPTP is much more protonated in the aqueous phase than in the organic phase, where the dimer and trimer are much more protonated than the monomer.[8]

TPTZ in very diluted aqueous HNO_3 (pH 2−5) forms the dimer $B_2H_2^{2+}$, which participates in the protonation equilibrium of TPTZ together with the monomeric species B, BH^+, and BH_2^{2+}. The formation constant of the dimer is $[B_2H_2^{2+}][H_2B^{2+}]^{-1}[B]_0^{-1} = (1.8 \pm 0.2) \times 10^4$, with $[B]_0$ denoting the solubility of TPTZ in distilled water.[33]

2.6. Configuration

2.6.1. Terpy

A tautomeric mixture of symmetric and asymmetric BH^+ species is formed in the first step of the protonation of terpy in aqueous solutions. Unlike this, only a symmetrical species BH_2^{2+} is assumed to be formed in the second protonation step, because two H^+ ions cannot be accommodated at adjacent N atoms. The second protonation step is not expected to include any intermediate intermolecular transfiguration, and BH_2^{2+} is supposed to be formed directly from asymmetrical BH^+.[14]

Elsewhere it is supposed that the formation of symmetric BH^+ species of terpy is sterically restricted and only lateral pyridyl nitrogen atoms are protonated in the stepwise protonation of B to BH_2^{2+}.[34] Ultraviolet spectra show that unprotonated terpy adopts predominantly the *trans*−*trans* configuration in cyclohexane, chloroform, ethanol, and water at pH 12. Monoprotonated *cis*−*trans* configuration is adopted in water at pH 4, and diprotonated *cis*−*cis* configuration predominates in water at pH 1.8.[35] This might be in agreement with quantum mechanics calculations, which predict the optimum configurations as *cis*−*trans* for the monoprotonated form (generally expected to predominate at pH 4) and *cis*−*cis* for the diprotonated form (expected to predominate at pH 1.8).[36] No indication of an intramolecular $N\cdots H^+-N$ link in the protonated form is said to exist,[35] but its formation is implied by calculations.[36]

As for nonprotonated terpy, only an indication has been found that in D_2O the terminal pyridyl rings are identical on the NMR time scale. However, it is not possible to distinguish between the *cis*−*cis* and *trans*−*trans* configurations, which both possess C_{2v} symmetry.[37] The *trans*−*trans* configuration was found in solid 4′-dimethylaminoterpy but, contrary to terpy, the side rings deviate from strict planarity by 7.4°.[38]

Quantum mechanics calculations predict for unprotonated terpy the energy order *trans*−*trans* < *cis*−*trans* < *cis*−*cis*. The *trans*−*trans* configuration is perfectly planar. In the *cis*−*trans* configuration the *trans* ring is nearly planar (torsion angle −176.1°), while the *cis* ring is twisted by −43.0° from planarity. In the *cis*−*cis* configuration, the lateral rings are twisted by −47.9°. The twisting is ascribed to repulsion between lone electron pairs on vicinal N atoms.[36]

2.6.2. Other Ligands

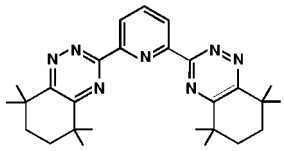
2,2′:6′,2″:6″,2‴-Quaterpyridyl is indicated by ^1H NMR to favor in $CDCl_3$ an arrangement involving twisting about the interannular bonds. The diprotonated ligand adopts in CD_3CN an average C_2 symmetry on the NMR time scale.[39]

2,6-Bis[1-(1-(*S*)-neopentyl)benzimidazol-2-yl]pyridine is indicated by ^1H NMR to have a C_2 symmetry and a *trans*−*trans* configuration in CD_3CN. Such configuration also prevails in the solid state, where the benzimidazole moieties are twisted by 23°−27° with regard to the plane of the pyridine ring.[26] 4-Carboxy-2,6-bis(1-methylbenzimidazol-2-yl)pyridine (*S*)-neopentyl ester exhibits chirality arising from the asymmetric carbon atom. Its specific rotary dispersion at 25 °C in degassed anhydrous acetonitrile is 8.1 deg dm^2 mol^{-1}.[40]

The energy of various configurations of unprotonated 2,6-di(2-benzoxazolyl)pyridine (related to N atoms) is predicted by quantum mechanics calculations to increase in the order *trans*−*trans* < *cis*−*trans* < *cis*−*cis*. The monoprotonated ligand is said to have five low-energy configurations with the protonated site being either the pyridine (py) or benzoxazole (bo) ring. The configurations are *cis*−*cis* (py), *cis*−*trans* (bo), *cis*−*cis* (bo), *cis*−*trans* (py), and *trans*−*trans* (py). The configuration *cis*−*cis* (py) is the lowest energy structure, and it is the only one that allows the formation of an intramolecular hydrogen bridge $N(py)\cdots H\cdots N(bo)$. Finally, the diprotonated ligand has three low-energy configurations, namely, *cis*−*cis*, *cis*−*trans*, and *trans*−*trans*, all of them being protonated at the two benzoxazole rings.[41]

In BTP type compounds, the order of energy of various configurations (related to 2-N atoms) has been predicted by quantum mechanics calculations to be *trans*−*trans* < *cis*−*trans* < *cis*−*cis*. The compounds are 2,6-bis(1,2,4-

triazin-3-yl)pyridine, 2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)pyridine,



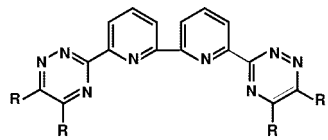
2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetra hydrobenzo-1,2,4-triazin-3-yl)pyridine

and 2,6-bis(9,9,10,10-tetramethyl-9,10-dihydrobenzo-1,2,4-triazaanthrane-3-yl)pyridine. In the monoprotonated form, the H^+ ion is bound to the pyridyl N atom and the energy order is *cis*−*cis* < *trans*−*trans* < *cis*−*trans*. When the ligands become diprotonated, the H^+ ion from the pyridyl N atom is migrated to the 2-N atom of one of the triazine rings and the second H^+ ion is bound to the 1-N or 2-N atom of another triazine ring.[42]

6-(1,2,4-Triazin-3-yl)-2,2′-bipyridyl is predicted by quantum mechanics calculations to possess the lowest energy in the *trans*−*trans* configuration, in which the N atom of the lateral pyridyl ring and the 2-N atom of the triazinyl ring are in *trans* positions. Only a slightly higher energy is predicted for the *cis*−*trans* configuration in which the N atom of the lateral pyridyl ring is in the *trans* position and the 2-N triazinyl atom is in the *cis* position. With this position designation, that is, with the first specifier designating the position of the pyridyl N atom and the second specifier designation the position of the 2-N triazinyl atom, the energy of the nonprotonated configurations increases in the order *trans*−*trans* < *trans*−*cis* < *cis*−*trans* < *cis*−*cis*. If the molecule is monoprotonated, the lowest energy protonation site is always the N atom of the central pyridine ring. The energy of various protonated configurations increases in the order *cis*−*cis* < *cis*−*trans* < *trans*−*cis* < *trans*−*trans*.[43]

Two sets of configurations are predicted by DFT calculations on the tetradentate ligand 6,6′-bis(1,2,4-triazin-3-yl)-2,2′-bipyridyl.

One of them includes configurations with the pyridine rings



R	
H	6,6'-di(1,2,4-triazin-3-yl)-2,2'-bipyridyl
alkyl	6,6'-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridyl (alkyl = methyl, ethyl, and pentyl)

in a *trans* position. They possess low energy, which in gas phase and solvents with low dielectric constants increases in the order *trans*−*trans*−*trans* < *cis*−*trans*−*trans* < *cis*−*trans*−*cis*. The another set are configurations with the pyridine rings in a *cis* position, the energy of which increases in the order *trans*−*cis*−*trans* < *trans*−*cis*−*cis* < *cis*−*cis*−*cis*. The ligand is first protonated at the N atom of one of the pyridine rings (1, 1′), and the low energy configurations are *trans*−*trans*−*cis* (1) < *trans*−*trans*−*cis* (1′) < *cis*−*cis*−*cis* (1) < *trans*−*cis*−*trans* (1).[44]

Energies in the gas phase predicted by quantum mechanics calculations for TPTZ decrease in the order *cis*−*cis* > *cis*−*trans* > *trans*−*trans*, while for 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine the order is *cis*−*cis* > *trans*−*trans* > *cis*−*trans*.[45]

2.7. Chemical and Radiation Stability

The stability is of general interest, but particular attention is focused on BTPs, which are very efficient in the separation of An(III) from Ln(III) but, unfortunately, not sufficiently stable in a radiation field and in contact with nitric acid. For example, if 0.04 M DPTP in TPH/1-octanol (7/3 v/v) is contacted with 1 M HNO_3, the DPTP fraction remaining unhydrolyzed is 59%, 18%, and 5% after 5, 22, and 26 days, respectively. The hydrolysis of DPTP is slower in chloroform and in argon atmosphere and faster at elevated temperature. The first hydrolysis step is attack on a CH_2 group born by one of the propyl substituents at the triazinyl ring. It results in the formation of a nitro compound, which is subsequently converted to an alcohol or a ketone. Attack on a CH_2 group born by a second propyl substituent results in the formation of dialcohols or diketones. DiPTP is more resistant to hydrolysis than DPTP. Its degradation is accelerated in the presence of nitrous acid and proceeds in similar steps as the hydrolysis of DPTP.[11]

Improvement of the hydrolytic stability by branching the alkyl substituents at the 5,6-positions of the triazinyl rings was also observed in the early work on BTPs, where DiBTP was found to be noticeably more resistant to hydrolysis than DPTP.[7] In a more detailed study, solutions of various BTPs in 1-octanol were contacted with 1 M HNO_3, and the rate of hydrolysis decreased in the order 4-methyl-2,6-bis(5,6-dicyclohexyl-1,2,4-triazin-3-yl)pyridine > DiPTP > DiBTP ≫ DPTP > 2,6-bis(5,6-dibutyl-1,2,4-triazin-3-yl)pyridine. Also the diluent can decelerate the hydrolysis of BTPs. For example, the rate of the hydrolysis of DPTP decreases in the order tetrachloroethane > nitrobenzene ≫ TPH/1-octanol (7/3 v/v) ≈ 1-octanol.[46]

Since alkyl substituents at the triazinyl ring appear to be the most sensitive sites in degradation reactions, the chemical stability of two BTPs containing condensed triazine rings was tested. Markedly improved chemical stability is exhibited by 2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)pyridine and 2,6-bis(9,9,10,10-tetramethyl-9,10-dihydro-1,2,4-triazaanthran-3-yl)pyridine, which are not hydrolyzed by boiling 3 M HNO_3 during 24 h.[42] 6,6′-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2′-bipyridyl in 1-octanol in the presence of *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-(2-hexoxyethyl)malonamide does not change its efficiency in the extraction of Am(III) and Eu(III) even after two months contact with 1 M HNO_3.[47]

Stability toward redox conversions is illustrated by behavior in polarography, predominantly studied in acetonitrile at 0.1 M Et_4NClO_4, Bu_4NClO_4, or Bu_4NPF_6. Terpy reacts in two steps, being oxidized at +1.45 and +2.30 V and reduced at about −1.8 and − 2.40 V[48,49] (all $E_{1/2}$ are recalculated to NHE). 4′-Phenylterpy exhibits a similar reduction potential, −1.8 V.[50] 2,6-Bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine and its 4-phenyl derivative are reduced at −1.7 V. The 4-dimethylamino derivative is also reduced at −1.7 V, but the first step of its reduction proceeds at −0.8 V. A 4-nitrophenyl substituent enhances the sensitivity toward reduction only in the second step, and the $E_{1/2}$ values are −0.7 and −1.2 V.[51]

More than 80% DPTP is radiolytically degraded after a dose of 100 kGy in 1-octanol.[42] Radiolytic degradation of DiPTP in 1-octanol in the absence of nitric acid or in contact with 0.5 M HNO_3 originates compounds formed by addition of one or two alcohol molecules onto DiPTP. The degradation rate decreases with increasing concentration of DiPTP

and is about the same in TPH/1-octanol (7/3 v/v) and in pure 1-octanol. Increase of the nitric acid concentration supports the radiolysis and additionally causes hydrolysis of DiPTP.[11]

Analogous to chemical stability, also the radiation stability of BTPs is expected to be enhanced by introducing condensed triazine rings. 2,6-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)pyridine was after an integrated dose of 100 kGy degraded to >80% in 1-octanol, but only to 15% in an unspecified mixture of 1-octanol and nitrobenzene. Still more stable is 2,6-bis(9,9,10,10-tetramethyl-9,10-dihydro-1,2,4-triazaanthran-3-yl)pyridine, which is not degraded in 1-octanol after 100 kGy.[11,42] As mentioned in ref 11 but not in ref 42, the radiolysis was studied in a binary system, where 2-(hexoxyethyl)-*N*,*N*′-dimethyl-*N*,*N*′-dioctylmalonamide was present in the organic phase and the aqueous phase contained 1 M HNO_3 and 0.05 M hydrazinium nitrate as a nitrite-sequestrating agent.

Radiolysis of DETP in 1-hexanol diluent suppresses the distribution ratio of Am(III) in its extraction from 0.01 M $HClO_4$ + 0.99 M $NaClO_4$. The decrease with increasing radiation dose is ascribed to the radiolysis of the organic phase and is largely inhibited if it contains ≥2.5% nitrobenzene. *tert*-Butylbenzene exhibits no inhibiting effect. The inhibition is ascribed to the ability of nitrobenzene to remove solvated electrons and α-hydroxyalkyl radicals, which are supposed to be important intermediates in the radiolysis of DETP.[52]

The effect of irradiation and aging of 6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl in the extraction from from 0.01 M HNO_3 + 0.99 M $NaNO_3$ depends on the diluent. With hexanol diluent, both D_{Am} and D_{Eu} decrease with a dose inceasing from 7 to 28 kGy, while aging for ≤1400 h without irradiation has no particular influence. If cyclohexanone is taken as a diluent, the D_{Am} value decreases visibly with increasing dose at 7−57 kGy, while D_{Eu} is only weakly suppressed. Somewhat unexpected, both D_{Am} and D_{Eu} decrease during aging without irradiation for 350−3000 h.[53]

Extraction with 6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2′-bipyridyl under similar conditions shows a different pattern. With both diluents, hexanol and cyclohexanone, the D_{Eu} remains practically unaffected by the irradiation at ≤13 kGy, while D_{Am} increases with the dose at 3−13 kGy. Aging without irradiation for ≤650 h influences neither *D* value.[53]

3. Complexation of Lanthanides(III) and Actinides(III)

3.1. Stability of the Complexes

Due to lipophilic character of the majority of studied complexants, stability constants of their complexes have mostly been measured in pure organic or mixed aqueous−organic media. The constants are gathered in Table 2 for bipy, terpy, and BTP type N-donor complexants and in Table 3 for other compounds. Notice in the tables that purely heterocyclic complexants have mostly been studied, and less attention has been paid to compounds derived from aliphatic amines.

Rather few stability constants have been determined at a constant ionic strength, and they can be taken as conditional concentration constants. In most cases the ionic medium is constituted by anions introduced with the starting Ln(III) or An(III) salt and by free or complexed Ln^{3+} cations, and the ionic strength is variable and unspecified. Constants determined in such systems are apparent values, possibly including competitive complexing of the Ln^{3+} ions by anions of the medium. H^+ ions played an unimportant role, because the protonation of the complexant was mostly negligible under the conditions of the measurements.

The potentiometric K_3 values of the complexes of 2,6-bis(1-methylbenzimidazol-2-yl)pyridine[55] {*61−63,65,66,70,72,73,75−77,79,81*}^{T3} are more precise than the spectrophotometric K_3 values from the same source {*60,64,68,69,71,74,78,80*}^{T3}. However, the latter were not corrected for the presence of water in acetonitrile and might be lower by 0.2 log units than those in strictly anhydrous medium. Neither corrected for the presence of water are the K_2 and K_3 values of the complexes of 2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine[55] {*89−97*}^{T3} and the K_3 values of the complexes of 4-(4-dimethylaminophenyl))-2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine[55] {*101−109*}^{T3}.

Water could also play a role in finding 1:3 complexes of tris(2-pyridylmethyl)amine {*150,151*}^{T3} and (2-pyridylmethyl/2-pyridylethyl)amines {*154−159*}^{T3} in acetonitrile (see section 3.2.5). The original source[54] does not say whether presence of water was carefully enough avoided, and the results are possibly distorted by hydrolysis of the complexes.

3.1.1. Dependence of the Complex Stability on the Properties of the Complexant Molecule and the Solvent Properties

Comparison of the K_1, K_2, and K_3 values of La(III), Eu(III), and Lu(III) complexes of terpy[70] {*4,8,12*}^{T2} and 4,4′,4″-tri-*tert*-butylterpy[70] {*16,18,20*}^{T2} reveals no trend that would characterize the effect of the substitution. The effect, if any, is too small to be demonstrated by the low accuracy constants. Alteration of the central ring has a nonuniform effect, as shown by comparison of complexes of 2,6-di(2-pyridyl)pyrimidine, terpy, and TPTZ. With La(III) and Eu(III), the order of stability of 1:1 complexes is TPTZ[24,62] (2.8 {*137*}^{T3}, 3.6 {*141*}^{T3}) > 2,6-di(2-pyridyl)pyrimidine[24] (1.9 {*113*}^{T3}, 2.6 {*144*}^{T3}) > terpy[24,62] (1.60 {*5*}^{T2}, 2.40{*10*}^{T2}) while with Lu(III) it is terpy[24,62] (2.90) {*13*}^{T2} > TPTZ[24,62] (2.70 {*144*}^{T3}) > 2,6-di(2-pyridyl)pyrimidine[24] (2.40) {*115*}^{T3}.

Within BTPs, the stability of lanthanide(III) complexes appears to increase with the length of the alkyl substituents at the triazinyl rings. The K_1 of DMTP complexes[24,62] of La(III) (2.20 {*25*}^{T2}), Eu(III) (2.90 {*32*}^{T2}), and Lu(III) (2.70 {*37*}^{T2}) is higher than the K_1 of 2,6-bis(1,2,4-triazin-3-yl)pyridine complexes[24] of La(III) (1.20 {*21*}^{T2}), Eu(III) (1.60 {*22*}^{T2}), and Lu(III) (1.50 {*23*}^{T2}), and the β_2 of the Eu(III) complex of DPTP (6.7^{80} {*40*}^{T2}) is somewhat higher that of the DMTP complex (6.3^{80} {*31*}^{T2}). Stabilization of the complexes by the branching of the propyl substituent at the triazinyl ring is demonstrated by the higher β_3 value of the DiPTP complex of Eu(III) (14.0^{80} {*47*}^{T2}) in comparison with that of DPTP (12.0^{80} {*40*}^{T2}).

The effect of substituents at the 1-position of the benzimidazolyl rings in di(2-benzimidazolyl)pyridines is illustrated by the K_3 value of La(III) complexes. It decreases in the substituent order methyl[55] (5.8 {*61*}^{T3}) > 1-*S*-neopentyl[26] (5.3 {*82*}^{T3}) > 3,5-dimethoxybenzyl[55] (2.2 {*89*}^{T3}), with the pyridyl ring remaining unsubstituted. 2,6-Bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine[55] {*89−97*}^{T3} forms less stable complexes than 2,6-bis(1-methylbenzimidazol-2-yl)pyridine[55] {*61−63,65−67,70,72,73,*

Table 2. Formation Constants of Lanthanide(III) and Actinide(III) complexes with bipy, terpy, and 2,6-Bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines[a]

no.	N-donor	M^{3+}	salt/ionic medium	solvent	T, °C	method	constant denomination and logarithm
1	bipy[59]	Ce^{3+}	(0.078 M I^-)	pyridine	21	NMR	K_1 0.60(5), K_2 1.89(5)
					−40	NMR	$K_3 \approx -0.1$
2		Nd^{3+}	(0.078 M I^-)	pyridine	21	NMR	β_2 2.92(7)
					−40	NMR	K_3 −0.7(1)
3		U^{3+}	(0.078 M I^-)	pyridine	21	NMR	K_1 1.04(8), K_2 2.11(6)
					−40	NMR	K_3 0.20(3)
4	terpy	La^{3+}	0.1 M Et_4NClO_4	anhydrous MeCN	20	sp	K_1 7.7(2), K_2 5.8(3), K_3 4.8(4)[70]
5			(≤0.03 M Cl^-)	75% MeOH	25	sp	K_1 1.60(5)[b,24,62]
6		Ce^{3+}	(<0.03 M triflate)	MeCN	23	NMR	K_3 0.9(1)[119]
7		Nd^{3+}	(<0.03 M triflate)	MeCN	23	NMR	K_3 1.63(1)[119]
8		Eu^{3+}	0.1 M Et_4NClO_4	anhydrous MeCN	20	sp	K_1 7.9(5), K_2 5.5(5), K_3 5.0(5)[70]
9			(≤0.08 M Cl^-)	H_2O	25	sp	K_1 2.8[24]
10			(≤0.03 M Cl^-)	75% MeOH	25	sp	K_1 2.4,[24] 2.50(5)[b,62]
11			1 M LiCl	80% MeOH	25	sp	K_1 2.5(1)[10]
12		Lu^{3+}	0.1 M Et_4NClO_4	anhydrous MeCN	20	sp	K_1 7.5(1), K_2 7.2(2), K_3 5.4(3)[70]
13			(≤0.03 M Cl^-)	76% MeOH	25	sp	K_1 2.90(5)[b,24,62]
14		U^{3+}	(<0.03 M triflate)	MeCN	23	NMR	K_3 2.5(3)[119]
15		Am^{3+}	(≤0.03 M Cl−)	75% MeOH	25	sp	K_1 3.4,[24,62] K_2 1.6[24]
16	4,4′,4″-tri-*tert*-butyl-terpy[70]	La^{3+}	0.1 M Et_4NClO_4	anhydrous MeCN	20	sp	K_1 7.6(5), K_2 6.4(7), K_3 4.4(7)
17			(≪0.001 M ClO_4^-)	anhydrous MeCN	20	NMR	K_2 4.7(7), K_3 3.1(5)
18		Eu^{3+}	0.1 M Et_4NClO_4	anhydrous MeCN	20	sp	K_1 9.6(1), K_2 5.7(2), K_3 3.8(3)
19			0.1 M Et_4NClO_4	anhydrous MeCN	20	NMR	K_2 5.3(8), K_3 2.8(4)
20		Lu^{3+}	0.1 M Et_4NClO_4	anhydrous MeCN	20	sp	K_1 8.7(5), K_2 6.7(6), K_3 5.4(6)
21	2,6-bis(1,2,4-triazin-3-yl)-pyridine	La^{3+}	(≤0.08 M Cl^-)	76% MeOH	25	sp	K_1 1.20(5)[b,24]
22		Eu^{3+}	(≤0.08 M Cl^-)	76% MeOH	25	sp	K_1 1.60(5)[b,24]
23		Lu^{3+}	(≤0.08 M Cl^-)	76% MeOH	25	sp	K_1 1.50(5)[b,24]
24	DMTP	La^{3+}	(≤0.03 M Cl^-)	75% MeOH	5	sp	K_1 1.96(5)[b]
25			(≤0.03 M Cl^-)	76% MeOH	25	sp	K_1 2.20(5)[b,24,62]
26			(≤0.03 M Cl^-)	75% MeOH	55	sp	K_1 2.01(5)[b]
27		Nd^{3+}	(≤0.03 M Cl^-)	75% MeOH	5	sp	K_1 2.90(5)[b]
28			(≤0.03 M Cl^-)	75% MeOH	55	sp	K_1 2.78(5)[b]
29		Eu^{3+}	(≤0.03 M Cl^-)	75% MeOH	5	sp	K_1 3.04(5)[b]
30			variable HCl	H_2O	25	sp	K_1 1.7[24]
31			$I \leq 0.0022$ (NO_3^-) pH 2.8−4.6	50%MeOH	ng	es-ms	K_1 2.9(2), K_2 3.4(1)[80]
32			(≤0.03 M Cl^-)	76% MeOH	25	sp	K_1 2.90(5)[b,24,62]
33			(≤0.03 M Cl^-)	75% MeOH	55	sp	K_1 2.85(5)[b]
34		Ho^{3+}	(≤0.03 M Cl^-)	76% MeOH	5	sp	K_1 2.47[b]
35			(≤0.03 M Cl^-)	75% MeOH	55	sp	K_1 2.42[b]
36		Lu^{3+}	(≤0.03 M Cl^-)	75% MeOH	5	sp	K_1 2.51(5)[b]
37			(≤0.03 M Cl^-)	76% MeOH	25	sp	K_1 2.70(5)[b,24,62]
38			(≤0.03 M Cl^-)	75% MeOH	55	sp	K_1 2.60(5)[b]
39		Am^{3+}	variable HCl	75% MeOH	25	sp	K_1 4.1,[24,62] K_2 2.9,[22] K_3 2.9[24]
40		Eu^{3+}	$I \leq 0.0022$ (NO_3^-) pH 2.8−4.6	50% MeOH	ng	es-ms	β_2 6.7(5), β_3 12.0(5)[80]
41	DiPTP[c]	La^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 11.7(1)
42		Ce^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 11.9(2)
43		Pr^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 12.3(2)
44		Nd^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 12.6(3)
45		Sm^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 13.9(3)
46		Eu^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 14.2(3)
47			$I \leq 0.0022$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 14.0(6)[80]
48			$I \leq 0.0022$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	trlil	β_3 14.3(6) (lifetime)[79] β_3 14.5(8) (spectrum)[79]
49		Gd^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 14.5(2)
50		Tb^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 15.4(2)

Table 2. Continued

no.	N-donor	M^{3+}	salt/ionic medium	solvent	T, °C	method	constant denomination and logarithm
51	DiPTP	Dy^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 15.6(2)
52		Ho^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 17.5(1.0)
53		Er^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 15.8(6)
54		Tm^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 17.0(6)
55		Yb^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 16.0(6)
56		Lu^{3+}	$I \leq 0.0019$ (NO_3^-) pH 2.8−4.6	50% MeOH	25	es-ms	β_3 16.7(8)

[a] Ionic medium in parentheses means ions were added with Ln^{3+} or An^{3+}. Methods: sp = UV/visible spectrophotometry; es-ms = electrospray mass spectrometry; trlil = time-resolved laser-induced luminiscence; NMR = NMR spectrometry. Other abbreviations: rt = unspecified room temperature; ng = not given, probably rt. Digit in parentheses after a constant denotes confidence limits of the last decimal place. $K_n = [MB_n^{z+}][M^{z+}]^{-1}[B]^{-n}$; $\beta_2 = K_1K_2$; $\beta_3 = K_1K_2K_3$. [b] From Thauvin, D. personal communication, 2000, cited in ref 56. [c] All but three β_3 values are from ref 81.

75−77,79,81}^{T3} not only with La(III) but also with other Ln(III) (Figure 3). The effect is ascribed to the presence of the bulky 3,5-dimethoxybenzyl substituents, which destabilize the *cis−cis* configuration through interaction with the hydrogen at the 5-position of the central pyridine ring. The substituents also make it difficult to provide a tight coordination cavity around the Ln^{3+} ion.

Another complexant with these bulky substituents at the benzimidazolyl ring, 4-(4-diethylaminophenyl)-2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine, forms much more stable lanthanide(III) complexes because of the presence of an electron-donating group at the 4-position of the central pyridine ring.[55] The effect of the 4-substitution can be illustrated with invariable 3,5-dimethoxybenzyl at the benzimidazolyl rings by the decrease of the K_3 value of the La(III) complex in the sequence 4-dimethylaminophenyl[55] (4.8 {*101*}^{T3}) > carboxyl esterified by 2-methylbutyl[40] (3.8 {*110*}^{T3}) > no 4-substituent[55] (2.2 {*89*}^{T3}). Some substituent effects in 2,6-di(2-benzimidazolyl)pyridines are exemplified for Ln(III) in Figure 3.

Only a vague picture of the effect of substituent and chirality on the stability of Eu(III) and Tb(III) complexes is given by data[54] on a sequence of amines carrying 2-pyridylmethyl (X) and 2-pyridylethyl (Y) substituents, namely, X_3N {*150,151*}^{T3}, (*R*)-X_2YN {*154,155*}^{T3}, (*R,R*)-XY_2N {*156,157*}^{T3}, and (*R,S*)-XY_2N {*158,159*}^{T3}. The paper[54] gives K_1 to K_3 values, although the formation of a 1:3 complex is fully questionable (see section 3.2.5). This could impair the determination of the K_1 and K_2 values. Even if it is admitted that K_1 values could be of acceptable reliability, only a decrease of K_1 in the above order is observed, which mostly lies within the accuracy limits.

Utilizing gas-phase quantum mechanics calculations, stability constants of [EuB^{3+}] complexes in 76% methanol can be correlated with the effective charges of the central and lateral N atoms of tridentate ligands (q_{Nc} and q_{Nl}, respectively). As a function of increasing q_{Nc}, the K_1 value decreases in the ligand order 4-amino-2,6-(2-pyridyl)-1,3,5-triazine > TPTZ > terpy > 2,6-di(2-pyridyl)pyrazine > 2,6-di(2-benzimidazolyl)pyridine > 2,6-bis(1,2,4-triazin-3-yl)pyridine. As a function of q_{Nl}, the K_1 value increases in the reversed ligand order, with the exception of the last ligand, the q_{Nl} value of which is exceptionally high. Similar correlations exist between the K_1 value and bond overlap populations (OP) in the $Eu-N_{central}$ and $Eu-N_{lateral}$ bonds. K_1 decreases with increasing OP($Eu-N_c$) in the above ligand order and increases with increasing OP($Eu-N_l$) in reversed ligand order. Covalent contribution to the Eu−N bond is understood to decrease in the above ligand order.[56]

Few data are available about the solvent effect. The log K_1 value of Eu(III) complexes was measured in H_2O/MeOH mixtures as a function of the volume fraction φ of MeOH, which was varied between 0% and 76%. The log K_1 of the terpy complex decreases linearly with increasing φ (cf. {*9,10*}^{T2}), log K_1 of the TPTZ complex increases linearly with φ (cf. {*139,141*}^{T3}), and log K_1 of the DMTP complex (cf. {*30,32*}^{T2}) increases concavely with φ.[24]

3.1.2. Dependencies of Stability Constants on the Atomic Number

Stability constants of complexes of 3,5-substituted triazine and several 2,6-substituted pyridines are shown in Figures 3 and 4 as functions of the atomic number Z of Ln(III). The figures demonstrate variations of the dependencies with the structure of the complexant. See in Figure 4 that Y(III) forms with 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine a somewhat weaker complex than Ln(III).

Noticeable is the decrease of the K_3 value with the atomic number of Ln(III) complexes of 2,6-bis(1-methylbenzimidazol-2-yl)pyridine in acetonitrile, observed for Gd(III) to Lu(III) (Figure 3, curve 1). It is ascribed to the diminishing of ionic radii of the Ln(III) with Z. To accommodate smaller Ln^{3+}, the cavity of the ligand has to shrink, but this induces large steric constraints. The Eu^{2+} ion can be easily accommodated by the cavity, because its ionic radius is larger by 0.18 Å than that of Eu^{3+}.[55]

Stability constants of 1:1 complexes of some tridentate N-donors were obtained by quantum mechanics calculations,[56] using three to four known constants as starting values. Figure 4 shows the calculated log K_1 vs Z curves for TPTZ and DMTP, together with the starting experimental K_1 values. Stability constants of complexes 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine and DMTP were calculated with the aid of K_1 of La(III), Eu(III), and Lu(III) complexes, and the other experimental K_1 values shown in Figure 4 have been published only more recently.[111] The agreement between the calculation and the experiment is quite good, and thus, the calculation appears to be a suitable tool for predicting stability constants.

Table 3. Formation Constants of Lanthanide(III) and Actinide(III) Complexes with Other Complexants in Acetonitrile (If Not Given Otherwise)[a]

no	N-donor	M^{3+}	ionic/salt medium	T, °C	method	constant denomination and logarithm
57	2,6-bis(2-benzimidazolyl) pyridine[c],[24]	$>La^{3+}$	(≤0.03 M Cl^-) 76% MeOH	25	sp	K_1 1.20(5)
58		Eu^{2+}	(≤0.03 M Cl^-) 76% MeOH	25	sp	K_1 1.70(5)
59		La^{3+}	(≤0.03 M Cl^-) 76% MeOH	25	sp	K_1 2.00(5)
60	2,6-bis(1-methylbenzimidazol-2-yl)pyridine[55]	La^{3+}	(<0.001 M ClO_4^-)	20	sp	K_1 8.9(3), K_2 7.9(4), K_3 6.5(6)
61			0.1 M Et_4NClO_4	25	pot	K_3 5.8(2)
62		Ce^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 6.0(1)
63		Pr^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 6.3(1)
64		Nd^{3+}	(<0.001 M ClO_4^-)	20	sp	K_1 8.7(2), K_2 7.2(4), K_3 7.3(6)
65			0.1 M Et_4NClO_4	25	pot	K_3 6.5(2)
66		Sm^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 6.4(2)
67		Eu^{2+}	0.1 M Et_4NClO_4	25	cv	β_3 ~15
68		Eu^{3+}	(<0.001 M ClO_4^-)	20	sp	K_1 9.0(2), K_2 6.7(3), K_3 6.9(4)
69		Gd^{3+}	(<0.001 M ClO_4^-)	20	sp	K_1 8.5(2), K_2 6.7(4), K_3 6.9(5)
70			0.1 M Et_4NClO_4	25	pot	K_3 6.6(2)
71		Tb^{3+}	(<0.001 M ClO_4^-)	20	sp	K_1 9.3(3), K_2 7.1(5), K_3 7.6(8)
72			0.1 M Et_4NClO_4	25	pot	K_3 6.1(1)
73		Dy^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 5.8(1)
74		Ho^{3+}	(<0.001 M ClO_4^-)	20	sp	K_1 8.9(3), K_2 7.3(5), K_3 6.1(6)
75			0.1 M Et_4NClO_4	25	pot	K_3 5.3(1)
76		Er^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 4.7(2)
77		Tm^{3+}	the same	25	pot	K_3 3.9(1)
78		Yb^{3+}	(<0.001 M ClO_4^-)	20	sp	K_1 9.4(5), K_2 7.1(6), K_3 5.2(7)
79			0.1 M Et_4NClO_4	25	pot	K_3 3.4(1)
80		Lu^{3+}	(<0.001 M ClO_4^-)	20	sp	K_1 9.0(4), K_2 6.4(4), K_3 4.9(5)
81			0.1 M Et_4NClO_4	25	pot	K_3 2.7(1)
82	2,6-bis[1-(1-*S*-neopentyl) benzimidazol-2-yl]pyridine	La^{3+}	0.1 M Et_4NClO_4	25	sp NMR	K_1 8.0(3), K_2 6.0(4), K_3 5.3(6)[26] K_1 8.1(1), K_2 5.7(5), K_3 1.2(2)[26]
83			0.1 M Et_4NClO_4	25	sp,lm	K_1 4.0(4)[b]
84		Eu^{3+}	0.1 M Et_4NClO_4	25	sp NMR	K_1 8.2(2), K_2 5.9(3), K_3 4.0(5)[26] K_1 8.2(2), K_2 5.9(3), K_3 0.9(1)[26]
85			0.1 M Et_4NClO_4	25	sp,lm	K_1 4.0(5)[b]
86		Tb3+	0.1 M Et_4NClO_4	25	sp,lm	K_1 4.0(5)[b]
87		Lu^{3+}	0.1 M Et_4NClO_4	25	sp NMR	K_1 8.0(2), K_2 6.1(3), K_3 4.3(5)[26] K_1 6.9(1), K_2 5.7(1)[26]
88			0.1 M Et_4NClO_4	25	sp,lm	K_1 6.4(2)[b]
89	2,6-bis[1-(3,5-dimethoxybenzyl) benzimidazol-2-yl] pyridine[55]	La^{3+}	0.1 M Et_4NClO_4	25	pot	K_2 5.0(1), K_3 2.2(2)
90		Ce^{3+}	0.1 M Et_4NClO_4	25	pot	K_2 4.8(1), K_3 2.9(3)
91		Pr^{3+}	0.1 M Et_4NClO_4	25	pot	K_2 4.9(1), K_3 2.8(1)
92		Nd^{3+}	0.1 M Et_4NClO_4	25	pot	K_2 4.9(1), K_3 3.2(2)
93		Sm^{3+}	0.1 M Et_4NClO_4	25	pot	K_2 5.5(1), K_3 3.6(1)
94		Gd^{3+}	0.1 M Et_4NClO_4	25	pot	K_2 4.8(1), K_3 3.2(1)
95		Tb^{3+}	0.1 M Et_4NClO_4	25	pot	K_2 4.9(1), K_3 3.1(1)
96		Er^{3+}	0.1 M Et_4NClO_4	25	pot	K_2 5.1(1), K_3 3.0(1)
97		Lu^{3+}	0.1 M Et_4NClO_4	25	pot	K_2 5.4(1), K_3 2.9(1)
98	ligand **A** (structural formulas **2**)[77]	La^{3+}	(<6×10^{-4} M NO_3^-) $MeCN/CH_2Cl_2$ (1/1)	20	sp	K_2 5.7(2)
99		Sm^{3+}	(<6×10^{-4} M NO_3^-) $MeCN/CH_2Cl_2$ (1/1)	20	sp	K_2 6.0(3)
100		Lu^{3+}	(<6×10^{-4} M NO_3^-) $MeCN/CH_2Cl_2$ (1/1)	20	sp	K_2 6.5(1)

Table 3. Continued

no	N-donor	M^{3+}	ionic/salt medium	T, °C	method	constant denomination and logarithm
101	4-(4-dimethylaminophenyl)-	La^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 4.8(2)
102	2,6-bis[1-(3,5-dimethoxybenzyl)	Pr^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 5.5(2)
103	benzimidazol-2-yl]pyridine[55]	Sm^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 6.0(1)
104		Gd^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 6.1(2)
105		Tb^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 5.9(1)
106		Dy^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 5.2(2)
107		Ho^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 4.8(2)
108		Tm^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 3.9(1)
109		Yb^{3+}	0.1 M Et_4NClO_4	25	pot	K_3 3.1(1)
110	4-carboxy-2,6-bis(1-methylbenzimidazol-2-yl)pyridine neopentyl ester[40]	La^{3+}	0.1 M Et_4NClO_4	25	sp NMR	K_1 7.8(4), K_2 6.0(5), K_3 3.8(6) K_1 8.0(2), K_2 6.0(3), K_3 3.8(3)
111		Eu^{3+}	0.1 M Et_4NClO_4	25	sp	K_1 8.0(3), K_2 6.4(4), K_3 4.6(5)
112		Lu^{3+}	0.1 M Et_4NClO_4	25	sp NMR	K_1 8.0(3), K_2 6.4(4), K_3 2.9(4) K_1 7.9(2), K_2 6.5(3), K_3 3.1(3)
113	2,6-di(2-pyridyl)	La^{3+}	(≤0.03 M Cl^-) 76% MeOH	25	sp	K_1 1.90(5)
114	pyrimidine[c,24]	Eu^{3+}	(≤0.03 M Cl^-) 76% MeOH	25	sp	K_1 2.60(5)
115		Lu^{3+}	(≤0.03 M Cl^-) 76% MeOH	25	sp	K_1 2.40(5)
1165		Am^{3+}	var. HCl in H_2O	25	sp	K_1 4.0, K_2 0.7
117	4-amino-2,6-di(2-pyridyl)-	La^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 3.85(2)
118	1,3,5-triazine (all but three		(≤0.03 M Cl^-) 76% MeOH	25	sp	K_1 3.90(5)[c,24]
119	K values from ref 111)	Ce^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.28(4)
120		Pr^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.43(1)
121		Nd^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.62(4)
122		Sm^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.62(3)
123		Eu^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.5(1)
124			(≤0.03 M Cl^-) 76% MeOH	25	sp	K_1 4.60(5)[c,24]
125		Gd^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.29(5)
126		Tb^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.15(6)
127		Dy^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.07(2)
128		Ho^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.05(3)
129		Er^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.10(5)
130		Tm^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.23(3)
131		Yb^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.30(3)
132		Lu^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 4.40(3)
133			(≤0.03 M Cl^-) 76% MeOH	25	sp	K_1 4.30(5)[c,24]
134		Y^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 3.6(1)
135		Am^{3+}	(≤0.033 M ClO_4^-) pH 5−5.5 75% MeOH	25	sp	K_1 5.8(1)
136	TPTZ	La^{3+}	(≤0.03 M Cl^-) 75% MeOH	5	sp	K_1 2.90(5)[c]
137			(≤0.03 M Cl^-) 75% MeOH	25	sp	K_1 2.80(5)[c,24,62]
138			(≤0.03 M Cl^-) 75% MeOH	55	sp	K_1 2.66(5)[c]
139		Eu^{3+}	var. HCl in H_2O	25	sp	K_1 2.7[24]
140			(≤0.03 M Cl^-) 75% MeOH	5	sp	K_1 3.68(5)[c]
141			(≤0.03 M Cl^-) 75% MeOH	25	sp	K_1 3.5,[24] 3.6(2),[62] 3.60(5)[c]
142			(≤0.03 M Cl^-) 75% MeOH	55	sp	K_1 3.18(5)[c]
143		Lu^{3+}	(≤0.03 M Cl^-) 75% MeOH	5	sp	K_1 2.76(5)[c]
144			(≤0.03 M Cl^-) 75% MeOH	25	sp	K_1 2.70(5)[c,24,62]
145			(≤0.03 M Cl^-) 75% MeOH	55	sp	K_1 2.67(5)[c]
146		Am^{3+}	(≤0.03 M Cl^-) 75% MeOH	25	sp	K_1 3.5,[24,62] K_2 1.0[24]
147	tris(2-pyridylmethyl)amine	La^{3+}	(low I^- in pyridine)	25	NMR	K_2 1.0(1)[88]
148		Nd^{3+}	(low Cl^- in D_2O)	25	NMR	K_1 2.40(4)[89]
149		Eu^{3+}	(low Cl^- in D_2O)	25	NMR	K_1 2.41(4)[89]
150			(≤0.0015 M triflate)	rt	sp	K_1 7.5(4), K_2 5.2(2), K_3 5.3(3)[54]
151		Tb^{3+}	(≤0.0015 M triflate)	rt	sp	K_1 8.1(2), K_2 5.4(2), K_3 5.4(1)[54]
152		Lu^{3+}	(low Cl^- in D_2O)	25	NMR	K_1 2.11(3)[89]
153		U^{3+}	(low I^- in pyridine)	25	NMR	K_2 1.10(7)[88]
154	(*R*)-[1-(2-pyridyl)ethyl]bis(2-pyridylmethyl)amine	Eu^{3+}	(≤0.0015 M triflate)	rt	sp	K_1 7.4(3), K_2 5.6(2), K_3 5.4(2)[54]
155		Tb^{3+}	(≤0.0015 M triflate)	rt	sp	K_1 7.9(4), K_2 5.3(2), K_3 5.8(3)[54]
156	(*R*,*R*)-bis[1-(2-pyridyl)ethyl](2-pyridylmethyl)amine	Eu^{3+}	(≤0.0015 M triflate)	rt	sp	K_1 6.9(2), K_2 5.3(3), K_3 5.6(1)[54]
157		Tb^{3+}	(≤0.0015 M triflate)	rt	sp	K_1 7.1(3), K_2 5.0(3), K_3 6.1(4)[54]

Table 3. Continued

no	N-donor	M^{3+}	ionic/salt medium	T, °C	method	constant denomination and logarithm
158	(*R*,*S*)-bis[1-(2-pyridyl)ethyl] (2-pyridylmethyl)amine	Eu^{3+}	(≤0.0015 M triflate)	rt	sp	K_1 6.7(3), K_2 5.5(4), K_3 5.7(5)[54]
159		Tb^{3+}	(≤0.0015 M triflate)	rt	sp	K_1 7.0(1), K_2 5.7(4), K_3 6.2(1)[54]
160	tris(2-pyrazylmethyl)amine	La^{3+}	(low I^- in pyridine)	25	NMR	K_1 2.27(5)[92]
161		U^{3+}	(low I^- in pyridine)	25	NMR	K_1 2.24(5)[92]
162		La^{3+}, U^{3+}	(low I^- in THF)	25	NMR	$K_{1(U)}/K_{1(La)}$ 0.52(7)[92]
163	tris(2-benzimidazolylmethyl) amine	La^{3+}	(low I^- in pyridine)	25	NMR	K_2/K_1 1.54(5)[88]
164			(low triflate in pyridine)	25	NMR	K_2/K_1 2.06(5)[88]
165			(low triflate)	25	NMR	K_2/K_1 −1.5[90]
166		Eu^{3+}	(low triflate)	25	NMR	K_2/K_1 1.15[90]
167		Lu^{3+}	(low triflate)	25	NMR	K_2/K_1 0.5[90]
168		U^{3+}	(low I^- in pyridine)	25	NMR	K_2/K_1 0.90(5)[88]

[a] Ionic medium in parentheses denotes ions added with Ln^{3+} or An^{3+}. Method: sp = UV/visible spectrophotometry; pot = potentiometric titration; NMR = NMR spectrometry; cv = cyclic voltammetry; lm = luminescence measurement;. rt = unspecified room temperature; ng = not given, probably rt. Digit in parentheses behind a constant is confidence limit of the last decimal place. $K_n = [MB_n^{z+}][M^{z+}]^{-1}[B]^{-n}$; $\beta_2 = K_1K_2$; $\beta_3 = K_1K_2K_3$; $\beta_{n,m} = [M_nB_m^{nz+}][M^{z+}]^{-n}[B]^{-m}$. [b] From Muller, G.; Maupin, C. L.; Riehl, J. P.; Birkedal, H.; Piguet, C.; Bünzli, J.-C. G. Eur. J. Inorg. Chem. 2003, 4065. [c] From Thauvin, D. personal communication, 2000, cited in ref 56.

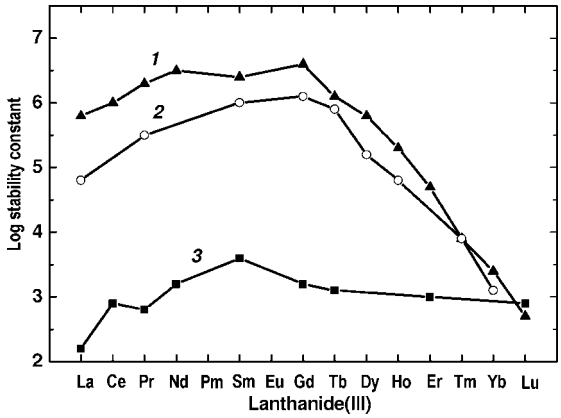


Figure 3. K_3 values of complexes of substituted dibenzimidazolyl pyridines[55] at 25 °C as functions of the atomic number of Ln(III): (1) 2,6-bis(1-methylbenzimidazol-2-yl)pyridine {*61*−*63,65*−*67,70,72,73,75*−*77,79,81*}[T3]; (2) 4-(4-dimethylaminophenyl)-2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine {*101*−*109*}[T3]; (3) 2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine {*89*−*97*}[T3].

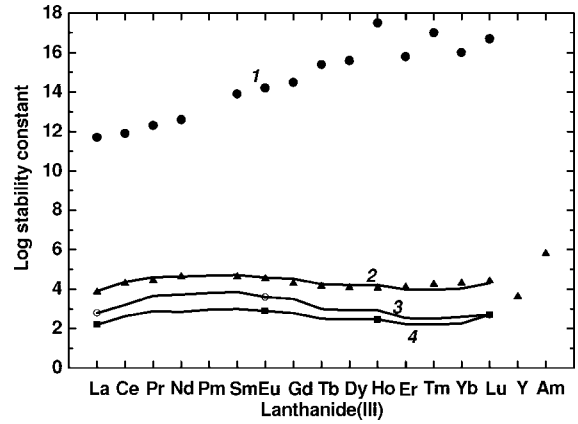


Figure 4. Stability constants of planar complexes as functions of the atomic number of Ln(III) at 25 °C. Experimental points: (1) β_3 of DiPTP complexes[81] in 50% MeOH at pH 2.8 {*41*−*47,49*−*56*}[T2]; (2) K_1 of complexes of 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine[111] in 75% MeOH {*117,119*−*123,125*−*132*}[T3]; (3) K_1 of TPTZ complexes[24,62] {*137,141,144*}[T3] in 76% MeOH; (4) K_1 of DMTP complexes[24,62] in 76% MeOH {*25,32,34,37*}[T2]. Lines are K_1 values calculated[56] for 76% MeOH.

3.1.3. Thermodynamics of the Complex Formation

Thermodynamic functions of the formation of some complexes are given in Table 4. They were determined from the temperature dependence of K_1 at 5−55 °C and β_3 at 11−77 °C. Let us notice that completely different ΔH and ΔS were calculated previously[56] for 4-amino-2,6-di-(2-pyridyl)-1,3,5-triazine using a donor−acceptor model.

Data in Table 4 can be evaluated according to a thermodynamic model[57] which predicts a correlation between ΔH and ΔS of the complexation reaction. The model perceives the complexation as a two-step process, involving dehydratation of the Ln^{3+} ion and a succeeding cation−ligand interaction. A $\Delta H-\Delta S$ correlation emerges if the free energy of dehydration is low but its contribution to ΔH and ΔS is much larger that that of the cation−ligand combination. The correlation also emerges if the contribution of the cation−ligand combination is approximately constant for a group of complexed ions.

No $\Delta H-\Delta S$ correlation is intimated in the formation of LnB^{3+} (Ln = La, Eu, and Lu) in the B series TPTZ−4-amino-2,6-di-(2-pyridyl)-1,3,5-triazine−DMTP (cf. data in Table 4). In series with variable complexed metal ion ($La^{3+}-Eu^{3+}-Lu^{3+}$) and constant B, there is no $\Delta H-\Delta S$ correlation with B = DMTP and TPTZ (Figure 5). An acceptable linear correlation is observed in the whole Ln(III) series with B = 4-amino-2,6-di-(2-pyridyl)-1,3,5-triazine (Figure 5). Finally, see in Table 4 that the complexation of Eu(III) by DiPTP is less exothermic in 50% MeOH than in octanol, where the desolvation energy plays a less important role.

Another thermodynamic model[58] assesses the cooperativity parameter u^{LL} in the self-assembly of mono- and bimetallic polynuclear complexes. When applied to a system involving only monocular 1:1 to 1:3 complexes of a nine-coordinated ion Ln^{3+} with a planar tridentate ligand, the model reduces to $\log u^{LL} = \log \beta_2 - \log 12 - 2 \log f$ and $\log u^{LL} = {}^1/_3(\log \beta_3 - \log 16 - 3\log f)$ with $\log f = \log K_1 - \log 3$. Somewhat awkward, both equations yield the same $\log u^{LL}$ value only if $\log K_2 = {}^1/_3 \log \beta_3$. Complete sets of K_1, K_2, and K_3 values are available for terpy[70] {*4,8,12*}[T2], 4,4′,4″-tri-*tert*-butylterpy[70] {*16,18,20*}[T2], 2,6-bis(1-methylbenzimidazol-2-yl)pyridine[55] {*60,64,68,69,71,74,78,80*}[T3], 2,6-bis[1-(1-*S*-neopentyl)benzimidazol-2-yl]pyridine[26] {*82,84,87*}[T3], and 4-carboxy-2,6-bis(1-methylbenzimidazol-2-yl)pyridine neo-

Table 4. Thermodynamic Functions of the Formation of Complexes with Some Planar Tridentate Ligands[a]

N-donor	M^{3+}	medium	const.	ΔG, kJ mol^{-1}	ΔH, kJ mol^{-1}	ΔS, J K^{-1} mol^{-1}
DMTP[62]	La^{3+}	75% MeOH	K_1 {25}^{T2}	−12.6	2.1	45
	Eu^{3+}		K_1 {32}^{T2}	−16.6	−6.8	34
	Lu^{3+}		K_1 {37}^{T2}	−15.4	3.2	59
DiPTP[79]	Eu^{3+}	50% MeOH, pH 2.8	β_3 {48}^{T2}	−84(2)	−29(3)	173(10)
		50% MeOH, pH 4.6	β_3 {48}^{T2}	−81(2)	−32(3)	164(10)
		1-octanol	β_3		−70(3)	
4-amino-2,6-di-(2-pyridyl)-1,3,5-triazine[b],[111]	La^{3+}	75% MeOH	K_1 {117}^{T2}	−22.0(1)	−13.5(3)	28(1)
	Ce^{3+}		K_1 {119}^{T2}	−24.4(2)	−16.4(6)	27(2)
	Pr^{3+}		K_1 {120}^{T2}	−25.3(1)	−17.5(7)	26(2)
	Nd^{3+}		K_1 {121}^{T2}	−26.4(3)	−19.6(7)	23(1)
	Sm^{3+}		K_1 {122}^{T2}	−26.4(2)	−21.0(4)	18(1)
	Eu^{3+}		K_1 {123}^{T2}	−25.7(6)	−20.4(7)	18(2)
	Gd^{3+}		K_1 {125}^{T2}	−24.5(3)	−18.0(8)	22(3)
	Tb^{3+}		K_1 {126}^{T2}	−23.7(4)	−14.4(6)	31(2)
	Dy^{3+}		K_1 {127}^{T2}	−23.2(2)	−12.0(4)	38(1)
	Ho^{3+}		K_1 {128}^{T2}	−23.1(2)	−8.8(6)	48(2)
	Er^{3+}		K_1 {129}^{T2}	−23.4(3)	−8.8(7)	49(2)
	Tm^{3+}		K_1 {130}^{T2}	−24.1(2)	−8.9(5)	51(2)
	Yb^{3+}		K_1 {131}^{T2}	−24.5(2)	−10.3(8)	48(3)
	Lu^{3+}		K_1 {132}^{T2}	−25.1(2)	−11.1(4)	47(1)
	Y^{3+}		K_1 {134}^{T2}	−20.6(6)	−6.7(5)	47(2)
	Am^{3+}		K_1 {135}^{T2}	−32.9(6)	−29(3)	14(10)
TPTZ[24,62]	La^{3+}	75% MeOH	K_1 {137}^{T2}	−16.0	−9.1	23
	Eu^{3+}		K_1 {141}^{T2}	−20.6	−18.6	4
	Lu^{3+}		K_1 {144}^{T2}	−15.4	−3.4	11

[a] ΔG and ΔS are given for 25 °C. Digit(s) in parentheses behind a value is confidence limit of the last decimal place(s). [b] Reevaluation of the original data by the present author yields somewhat higher ΔH and ΔS values (by 8−10%).

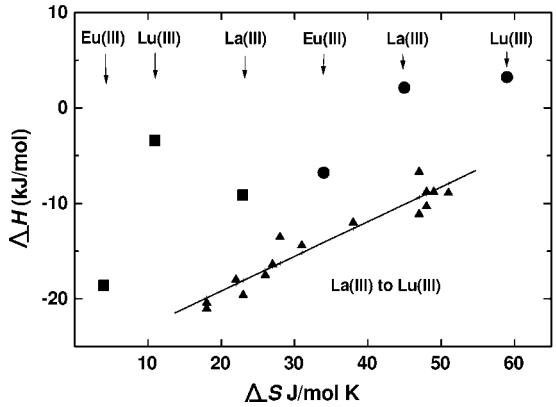


Figure 5. Enthalpy/entropy correlation in the complexation of families of Ln(III) by TPTZ (■), DMTP (●), and 4-amino-2,6-di-(2-pyridyl)-1,3,5-triazine (▲) (cf. Table 4).

pentyl ester[40] {110−112}^{T3}. They yield log u^{LL} values ranging from −4.0 to −0.4. However, the stability constants are so poorly accurate that the log u^{LL} values are subject to an uncertainty as high as ±0.4 to ±1.6 logarithmic units. This obscures eventual variations of log u^{LL} with the atomic number of Ln^{3+} and the ligand structure. The only implication of a variation is a decrease of log u^{LL} with increasing atomic number of Ln(III) in the complexation by 2,6-bis(1-methylbenzimidazol-2-yl)pyridine. The only certain conclusion is that log $u^{LL} < 0$, that is, the cooperativity is generally negative.

3.2. Composition, Structure, and Reactions of Complexes

Properties of lanthanide(III) and actinide(III) complexes other than their thermodynamic stability have been investigated in numerous studies. Due to the lipophilic nature of the studied complexants, the investigations have mostly been made in organic solvents, typically using NMR spectroscopy.

3.2.1. Polypyridyls and Their Derivatives

Bipy with Ce(III), Nd(III), and U(III), initially present as 0.01 M $MI_3(C_6H_5N)_4$ in anhydrous pyridine, forms a mixture of 1:1 and 1:2 complexes at $n = [B]_{tot}/[M(III)]_{tot} \leq 7$, while a 1:2 complex is the predominating species at $n \geq 8$. Complexes at 1:3 ratio have been detected only at −40 °C.[59]

Reaction of initially 0.00532 M $La(NO_3)_3 \cdot 6H_2O$ with terpy in acetonitrile at $n = [B]_{tot}/[La]_{tot} < 1$ produces an equilibrium of the complexes $[LaB(MeCN)(NO_3)_3]$ and $[LaB(H_2O)(NO_3)_3]$. The coordination number of La^{3+} in the complexes is 10, with B bound as a tridentate ligand and the nitrate groups bound as bidentate ligands. Two 1:2 species, indicated to be $[LaB_2^{3+}]$ and $[LaB_2(NO_3)_2^{+}]$, are formed at $n > 1$, and they coexist with the 1:1 complex $[LaB(NO_3)^{2+}]$. Anionic complexes, such as $[LaB(CH_3CN)(NO_3)_4^{-}]$ and $[LaB(H_2O)(NO_3)_4^{-}]$ act as counterions.[60]

Hydrated $M(NO_3)_3$ (M = Yb and Lu) compounds form with terpy in dry acetonitrile the complexes $[MB(NO_3)_3]$. Reaction in dry ethanol gives the complexes $[MB(EtOH)(NO_3)_3]$, in which the equatorial nitrate ion, that is, that lying in the same plane as terpy, becomes monodentate and forms a hydrogen bond to the O atom of an ethanol molecule. In wet ethanol or in water, the equatorial nitrate ion is completely replaced from the coordination sphere, and the complexes $[YbB(H_2O)_2(NO_3)_2^{+}]$ and $[LuB(H_2O)(EtOH)(NO_3)_2^{+}]$ are formed.[61] A 1:1 complex of Eu(III) with terpy has a hydration number of 5.0 in 50 vol % ethanol.[62]

Ce(III), Nd(III), and U(III), when taken as 0.01 M $MI_3(C_6H_5N)_4$, with terpy at $n = [B]_{tot}/[M(III)]_{tot} = 0-2$ in pyridine form only 1:1 and 1:2 complexes. No 1:3 complex has been detected at $n > 2$, and coordinated terpy is not in mutual exchange with free terpy.[63] Terpy complexes at 1:3 are formed by initially 0.02 M LaI_3, 0.005 M CeI_3 and NdI_3, and 0.01 M $UI_3(C_5H_5N)_4$ in acetonitrile at $n = 3$ and 100 °C but are poorly soluble and deposit as $[MB_3^{3+}][I^-]_3$.[64]

Ce(III) and U(III) cyclopentadienyl iodides, $[M(Cp)_2I]$, react in THF with 1 equiv of terpy, forming the complexes $[MB(Cp)_2^+]$. Reaction with 0.5 equiv of terpy in THF converts only a half of the starting amount of $[M(Cp)_2I]$ to $[MB(Cp)_2^+]$, while the other half is converted to the counterion $[M(Cp)_2I_2^-]$. Such a conversion does not proceed in pyridine.[65]

Solutions of terpy and 2-bromodecanoic acid (HA) in *tert*-butylbenzene or TPH extract Eu(III) and Am(III) from 0.005−0.5 M HNO_3 in the form of the complexes $[MBA_3]$ and $[MB_2A_3]$. The molecular complex $(HA)_2 \cdot B$ is the species that reacts with the M^{3+} ions.[21] 1-(2-Thienyl)-4,4,4-trifluoro-1,3-butanedione (thenoyltrifluoroacetone, HA) in benzene extracts Ln(III) as $[MBA_3]$ at pH 2−4. This has been reported for La(III), Nd(III), Sm(III), Eu(III), Yb(III), and Lu(III),[66] as well as for Ho(III).[67]

Complexes of terpy at a 1:2 ratio with Ce(III), Nd(III), and U(III) are fluxional in solution, because the ligands are equivalent and symmetrical.[63] The terpy ligands in the complexes $[MB_3^{3+}]$ with M = La, Ce, and Nd are equivalent in acetonitrile and adopt a D_3 symmetrical arrangement.[64]

A spectroscopic study was made to disclose the configuration of terpy molecules in the 1:3 complex of Eu(III). The complex was supposed to be $[EuB_3^{3+}]$ in acetonitrile solutions, which had been obtained by dissolving solid $[EuB_3^{3+}][ClO_4^-]_3$. It was concluded that terpy could be bound to the Eu^{3+} ion in all three possible configurations, and it was determined that ~78% of the terpy was bound as a tridentate *cis*−*cis* ligand, ~16% as a bidentate *cis*−*trans* ligand, and ~6% as a monodentate *trans*−*trans* ligand. The coordination number of the Eu^{3+} ion was then ≤9, and the relative concentrations of the complexes at 0.01 M Eu(III) were eight-coordinate (one bidentate and two tridentate ligands) > nine-coordinate (three tridentate ligands) ≫ seven-coordinate (one monodentate and two tridentate ligands). Free coordination sites of the Eu^{3+} ion were supposed to be occupied by acetonitrile molecules.[68]

However, results reported in ref 68 have more recently been reexaminated,[69] and only nine-coordinated species with three *cis*−*cis* terpy molecules have been found. It has been observed that in the presence of small amounts of water one of the Eu−N bonds is interrupted by a water molecule entering the coordination sphere of the Eu^{3+} ion in a fraction of the complex. This evokes the appearance of peaks that are very similar to those assigned in ref 68 to seven- and eight-coordinate isomers of the complex. The partial replacement of the N atom of one of the terpy molecules from the coordination sphere by water is possibly associated with rotation of the respective pyridine ring about an interpyridyl bond.

To fix the *cis*−*cis* configuration of the terpy moiety, $-(CH_2)_x-$ bridges were imposed between its 3,3′ and 5′−3″ positions. The ligands with $x = 2$ and 3 readily form complexes $[EuB_3^{3+}]$ in acetonitrile, but no complexation occurs at $x = 4$. Contrary to the terpy complex, the complexes of the bridged ligands adopt a nonplanar structure, which is more pronounced at $x = 3$ than at $x = 2$. With $x = 2$, the geminal positions of the bridges are equilibrating, due to conformational inversion of the bound ligand (the inversion is to some extent sterically inhibited if a *p*-tolyl substituent is introduced at the 4′-position). On cooling, conformational rigidity is achieved at −40 °C. Bridges with $x = 3$ are not equivalent, and the methylene group closest to the central pyridyl is the most inflexible. Conformational rigidity is achieved at +21 °C.[69]

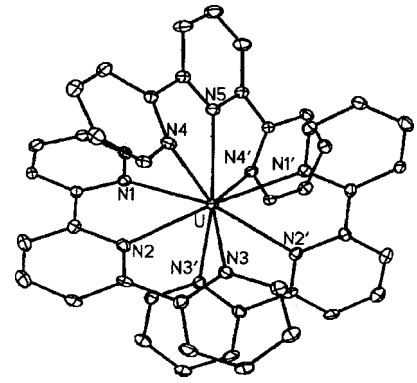


Figure 6. View of the structure of the cation in a crystal of the terpy complex $[UB_3^{3+}][I^-]_3 \cdot 2MeCN$ with displacement ellipsoids at the 30% probability level. Reproduced by permission of The Royal Society of Chemistry (Copyright 2002) from ref 64.

The $[EuB_3^{3+}]$ complex formed by a ligand that includes a −CH=CH− bridge between the 3,3′ positions and a $-CH_2-CH_2-$ bridge between the 5′−3″ positions exhibits a higher conformational mobility than the above complexes. Contrary to the above ligands, this one does not possess a symmetry axis through the 4-C and N atoms of the central ring. Thus, two possible isomers of the complex $[EuB_3^{3+}]$ can potentially be formed, but only that with a more symmetrical arrangement of the ligands about the Eu^{3+} ion was found. The dimethylene bridge remains unchanged down to −40 °C, and the other half of the ligand is virtually planar, causing the whole ligand to prefer a more planar conformation.[69]

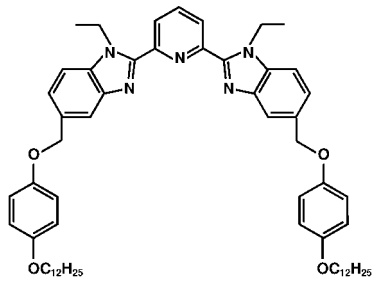
An example of the structure of a 1:3 terpy complex in a solid crystal is given in Figure 6. Complexes of Ln(III) with other planar tridentate ligands exhibit a similar structure, in which no other ligands are accommodated. Contrary to that, free coordination sites in 1:1 and 1:2 complexes are occupied by anions or molecules of solvent. Examples in Figure 7 show terpy complexes including nitrate anions. Notice that the anions are bound bidentately even if the coordination number of the central Ln^{3+} ion becomes >9.

Cyclic voltammetry in acetonitrile indicates that 4,4′,4″-triethylterpy and 4,4′,4″-tri-*tert*-butylterpy prefer Eu(III) over Eu(II) much more than terpy.[70]

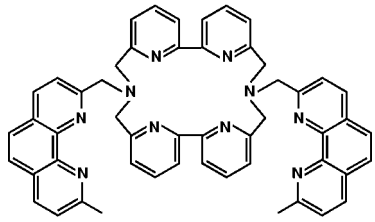
2,2′:6′,2″:6″,2‴-Quaterpyridyl forms only 1:1 complexes with Y(III) in methanol. The exact composition of a complex formed by YCl_3 is unknown, but it is indicated to be highly symmetrical on the ^1H NMR time scale, with the ligand acting as a symmetrical quaterdentate. A complex formed by $Y(NO_3)_3$ is substantially different, and its composition is indicated to be $[YB(NO_3)_2^+]$. In solid state, it contains both ionic and bidentately coordinated nitrate groups.[71]

6-(5,6-Dimethyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl forms mainly a 1:1 complex with La(III) in acetonitrile, with some indication of a 1:2 complex. Y(III) forms both 1:1 and 1:2 complexes at $n = [B]_{tot}/[Y(III)]_{tot} < 1.2$, and only a 1:2 complex is formed at $n > 1.2$. Am(III) is extracted from 0.01−0.1 M HNO_3 into a TPH solution of the ligand and 2-bromodecanoic acid (HA) as the complex $[AmB_3A_3]$.[43]

Ligand **B** (structural formulas **2**) forms 1:1 complexes with Eu(III) and Tb(III), which do not decompose in water and methanol due to their kinetic inertness. The complexation is more stable in water, where the interaction between Ln^{3+} and the phenanthroline branches is stronger.[72]



Ligand A



Ligand B

Structural formulas **2**

3.2.2. Substituted Di(benzimidazolyl)pyridines

The cation $[EuB_3^{3+}]$ with B = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine is formed in acetonitrile[73] and remains undissociated in a solution that is obtained by dissolving solid $[EuB_3^{3+}][ClO_4^-]_3$.[74] In contrast, for example, to DiPTP, which does not form complexes lower than 1:3, all successive 1:1, 1:2, and 1:3 complexes of Ln(III) are formed in acetonitrile stepwise by the above ligand,[55,75] 2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine,[55] 4-(4-diethylaminophenyl)-2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine,[55] and 2,6-bis[1-(1-*S*-neopentyl)benzimidazol-2-yl)pyridine.[26]

When solids of the type $[MB_3^{3+}][ClO_4^-]\cdot xH_2O$ (M = La and Eu) are dissolved in acetonitrile to a concentration of 0.005 M, with B = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine the complex $[LaB_3^{3+}]$ and the pseudo-D_3 complex $[EuB_3^{3+}]$ are the only significant species. With B = 2,6-bis(1-propylbenzimidazol-2-yl)pyridine, a 12% and an 8−10% fraction of minor species is present in the solutions of the La(III) and Eu(III) complexes, respectively. With B = 2,6-bis[1-(3,5-dimethoxybenzyl)benzimidazol-2-yl]pyridine, the fraction of minor species in the solution of $[EuB_3^{3+}]$ is as high as 30%.[75]

The $[CeB_3^{3+}]$ to $[DyB_3^{3+}]$ complexes of 2,6-bis(1-*R*-benzimidazol-2-yl)pyridine with the substituent R being methyl are isostructural in acetonitrile and adopt a D_3 symmetry. The triple-helical structure found in solids is retained also in solution, even if with a slight straightening of the coordinated ligand along the C_3 axis.[55] Also the complexes $[EuB_3^{3+}]$ and $[TbB_3^{3+}]$ with ligands bearing R = ethyl, propyl, and 3,5-dimethoxybenzyl are triple-helical in acetonitrile with a D_3 symmetrical structure on the NMR time scale. The ligand with R = methyl differs in its arrangement around the Eu^{3+} ion from the other ligands, indicating that the bulkier substituents affect the wrapping of the ligands around metal ions in solution.[76]

Lu(III) with 2,6-bis(1-methylbenzimidazol-2-yl)pyridine forms a 1:3 complex, but also a 1:2 complex is significant. When the solid form of the latter, $[LuB_2(MeOH)(H_2O)^{3+}][ClO_4)_3^-]_3\cdot 3MeOH$, is dissolved in acetonitrile, the ligands B are equivalent on the NMR time scale, and the methanol molecules undergo rapid exchange with the solvent.[75]

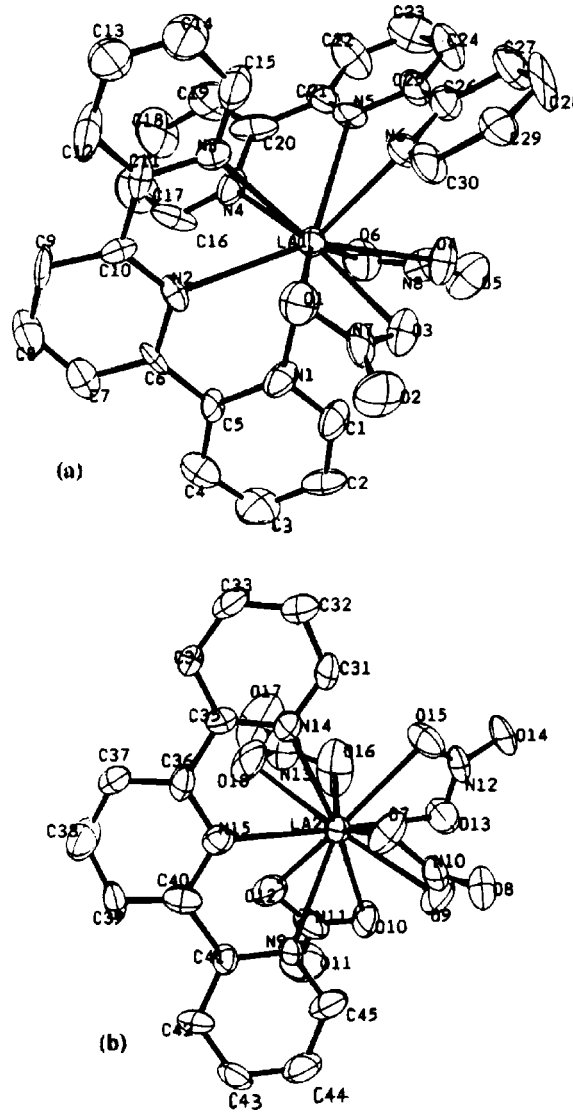


Figure 7. ORTEP drawing of the cation and the anion in $[LaB_2(NO_3)_2^+][LaB(NO_3)_4^-]$.[60]

4-Carboxy-2,6-bis(1-methylbenzimidazol-2-yl)pyridine (*S*)-neopentyl ester exhibits a strong tendency to form helical complexes with Ln(III). Electrospray mass spectrometry indicates the formation of 1:2 to 1:4 complexes with La(III) and Eu(III) in acetonitrile at $n = [B]_{tot}/[M(III)]_{tot} = 1-3$, but only 1:2 and 1:3 complexes with Lu(III). La(III) is more able to form a 1:3 complex from the 1:2 complex than Eu(III) and Lu(III), because the bulky 2-methylbutyl ester group strengthens the steric constraint in triple helical complexes of smaller lanthanide ions. ^{1}H NMR and spectrophotometry evidence only 1:1 to 1:3 complexes of La(III) and Eu(III), and it is suggested that the fourth ligand molecule is located in the outer coordination sphere. The specific rotatory dispersion of the complexes $[LaB_3^{3+}]$ and $[EuB_3^{3+}]$ (0.001 M in anhydrous MeCN) is 33.5 and 31.0 deg dm^2 mol^{-1}, respectively. It is four times larger that that of the free ligand, and this is ascribed to the triple helical structure of the complexes in the solution.[40]

Ligand **A** (structural formulas **2**) with La(III), Sm(III), Eu(III), and Lu(III) forms only the complex $[MB(H_2O)_x(NO_3)_3]$ with $x = 0-3$, which has been found in a 1/1 mixture of acetonitrile and CH_2Cl_2 and in acetonitrile

and chloroform ($n = [B]_{tot}/[M(III)]_{tot} \leq 25$ at 10^{-4} M ligand).[77] The ligand is tridentate in the complexes, which exist in chloroform and acetonitrile as mixtures of two closely related C_{2v}-symmetrical species, which do not interconvert on the NMR time scale at room temperature. The species appear to be in thermodynamic equilibrium, and the ratios of their concentrations depend on the solvent used, temperature, and the metal ion.[77]

3.2.3. Substituted Di(triazinyl)pyridines and Di(triazinyl)bipyridyl

DMTP with initially 0.01 M UI_3 forms in pyridine only the complex $[UB_3^{3+}]$ at $n = [B]_{tot}/[U(III)]_{tot} = 1-3$. In contrast, Ce(III) forms the complexes $[CeB_2^{3+}]$ and $[CeB_3^{3+}]$ at $n = [B]_{tot}/[Ce(III)]_{tot} = 2-3$. The DMTP ligands in the complex $[UB_3^{3+}]$ are equivalent in acetonitrile and adopt a D_3 symmetrical arrangement.[99] The same symmetry is indicated for Eu(III) complexes of DMTP, DPTP, and DiPTP in 50% methanol.[79] Relaxation titration reveals only the formation of a 1:3 complex of Gd(III) with DMTP in anhydrous acetone.[42]

The trisolvate complexes $MB_3(NO_3)_3 \cdot HNO_3$ with M = Am and Eu are formed in the extraction of trace metals by 0.03 M DPTP in TPH/2-ethyl-1-hexanol (4/1 v/v) from 1.9 M $(H,NH_4)NO_3$.[8] DPTP trisolvates of Am(III),[19] as well as of Cm(III) and Eu(III),[78] are exclusively formed in the extraction of Am(III) by 0.01−0.04 M DPTP in TPH/1-octanol (7/3 v/v) from 0.1−0.5 M HNO_3 and in the extraction of Cm(III) and Eu(III) by 0.025 M DPTP in TPH/1-octanol (7/3 v/v) from 0.01 M HNO_3 + 2.0 M $NaNO_3$. Cm(III) forms only a trisolvate also at a free DPTP concentration as low as 1×10^{-6} M. Contrary to this, Eu(III) forms exclusively a trisolvate only at >0.001 M free DPTP and a mixture of the 1:3 and lower complexes is formed at 0.0001 to 0.001 M free DPTP. Neither the Cm(III) complex nor the Eu(III) one contain coordinated nitrate ions.

The complex formation of Eu(III) with DMTP, DPTP, and DiPTP in 50% methanol was studied by electrospray mass spectrometry at $n = [B]_{tot}/[Eu(III)]_{tot} = 0.1-5$ and pH 2.8−4.6. The tendency of the ligands to form complexes stepwise decreases in the order DMTP > DPTP > DiPTP, that is, with the length and branching of the alkyl substituent at the triazinyl ring. DMTP forms 1:1, 1:2, and 1:3 complexes with Eu(III), DPTP forms only 1:2 and 1:3 complexes, and DiPTP forms exclusively 1:3 complexes without appearance of 1:1 and 1:2 complexes at low ligand to metal concentration ratios.[79−81] A 1:1 complex of Eu(III) with DMTP is hydrated in 50 vol % ethanol to a hydration number of $n_h = 5.6$, while a 1:2 complex is practically not hydrated ($n_h = 0.3$).[62]

The equilibrium in a solution of Eu(III) and DMTP in 50% methanol is shifted in favor of a 1:3 complex when the pH value is increased from 3.7 to 4.6, while the formation of 1:1 and 1:2 complexes is suppressed. With DPTP, the trend is reversed. When the pH value is increased from 2.8 to 4.6, the fraction of a 1:3 species decreases and that of a 1:2 species increases, while no 1:1 species is formed. DiPTP forms only 1:3 species at pH 2.8−4.6. The unique ability of DMTP to form a 1:1 complex with Eu(III) is ascribed to the less lipophilic character of the ligand, which facilitates the formation of hydrogen bonds of the complex with solvent molecules, unlike DPTP and DiPTP.[80]

The ability of BTPs to form lanthanide(III) and actinide(III) complexes as high as 1:3 is rare among tridentate N-donors. This ability makes them different, for example, from terpy, TPTZ, and 2,6-di(benztriazolyl)pyridines, which do not form complexes higher than 1:2. This ability of BTPs is explained by their hydrophobic exterior or an unusual distribution of the electron density in the ligand molecule.[81,82] According to quantum chemistry calculations, it also can play a role that the central ring of BTP is positively charged.[56]

An especially marked hydrophobic exterior and unusual distribution of the electron density may explain the lack of successive complex formation by DiPTP, which does not form lower Ln(III) complexes than 1:3. The electrostatic character of the complexes is evidenced by monotonous increase of their stability with the atomic number of the Ln (see Figure 4), in which steric factors are indicated to play an insignificant role.[81] Enthalpy is the driving force of the formation of the Eu(III) complex of DiPTP in 50% methanol.[79]

Relaxation titration clearly indicates the formation of only a 1:3 complex of 2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)pyridine with Gd(III) in acetonitrile. ^{1}NMR titration shows that La(III) can form 1:1, 1:2, and 1:3 complexes in acetonitrile, depending on the initial ligand to La(III) ratio (both titrations were performed at unspecified starting concentrations).[42]

In a homogeneous system, La(III) nitrate forms at least two complexes with 6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl in a 38/62 mixture of deuterated chloroform and MeCN. Free ligand and a 1:2 complex are present at $n = [B]_{tot}/[La(III)]_{tot} \geq 2$, where NMR spectrometry cannot distinguish between $[LaB_2^{3+}]$, $[La(H_2O)B_2^{3+}]$, and $[LaB_2(NO_3)^{2+}]$. The 1:2 complex is gradually converted to a 1:1 complex at $n \leq 2$.[44] Gd(III) forms only a 1:2 complex with a similar ligand, 6,6′-bis(5,6-dimethyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl, as evidenced by relaxation titration.[42]

In a binary phase system, 6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl in kerosene/1-octanol (7/3 v/v) extracts Am(III) and Eu(III) from 0.1−1.0 M HNO_3 as 1:2 complexes. It is supposed that the composition of the extracted complexes is $MB_2(NO_3)_3$, even if the slope of the log D_M vs log $[HNO_3]$ dependence is 2. The deviation from a slope of 3 is ascribed to partial protonation of the ligand.[83] Dissolved in cyclohexanone diluent, the ligand extracts 1:2 complexes of Am(III), Cm(III), Cf(III), and Eu(III) from 0.5 M HNO_3 + 0.5 M $NaNO_3$.[84] A mixture of a 1:1 and a 1:2 complexes is said to be formed in the extraction of Am(III) and Eu(III) by the complexant in anisole and tetrachloroethane from 0.01 M HNO_3 + 0.99 M $NaNO_3$.[85]

6,6′-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2′-bipyridyl forms a 1:2 complex with Gd(III) in acetonitrile.[42] A solution of the ligand in octanol extracts Am(III) in the presence of the *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-(2-hexoxyethyl)malonamide modifier as the complex $AmB_2(NO_3)_3$. Complexes at 1:2 ratios of Am(III) and Eu(III), presumably $MB_2(NO_3)_3$, are extracted in the absence of the amide.[47]

3.2.4. TPTZ

A 1:1 complex of Eu(III) with TPTZ is hydrated in 50 vol % ethanol. A hydration number of 5.6 has been found under the assumption that free Eu^{3+} ion is nonahydrated.[62] Both coordinating pyridyls of TPTZ are equivalent in species originated in the dissolution of solid $[PrB(OAc)_3]_2 \cdot 2MeOH$ and $[EuBCl_3(MeOH)_2] \cdot 2MeOH$ in methanol. This suggests that the complexes adopt a 2-fold symmetry, the methanol molecules undergo rapid exchange with the bulk solvent, and

noncoordinated pyridyl rotates rapidly around the C−C bond after breaking the hydrogen bonds with methanol. In the Eu(III) complex, the chloride ions exchange rapidly on the NMR time scale between different chloride positions. The dimeric form of the Pr(III) complex exchanges rapidly with a monomeric form.[86]

At 298 K, the complexed Eu^{3+} ion alternates among the three possible coordination positions at the TPTZ molecule. The process is slow on the NMR time scale. Two mechanisms can be considered: (1) complete dissociation of the Eu^{3+} ion from one coordinating position and subsequent reassociation at another position, and (2) partial dissociation of the Eu^{3+} ion, namely, from the triazine nitrogen and one of the pyridyl nitrogens, followed by rotation of the Eu^{3+}-bearing pyridyl group around the pyridyl−triazine bond and binding of the Eu^{3+} ion by another triazine and pyridyl nitrogen. The alternation of the Eu^{3+} ion is suggested to be based on the first mechanism.[86]

Contrary to terpy, TPTZ is able to extract An(III) at a pH value as low as 1. This is ascribed to the presence of as many as six basic N atoms in a TPTZ molecule. If TPTZ is mono- to triprotonated, still three vicinal N atoms can be left free so that the molecule can bind a M^{3+} ion as a tridentate ligand. On addition of an acid, a hydrogen ion is bound to the nitrogen of the pyridyl group not participating in binding M^{3+} and to an adjacent free nitrogen of the triazinyl ring. Further addition of acid protonates the nitrogen of one of the pyridyl groups bonding M^{3+}, leaving a bidentate coordination configuration for complexing the M^{3+} ion.[86]

3.2.5. Heterocycle-Substituted Aliphatic Amines

Reaction of initially 0.01 M La(III), Ce(III), Eu(III), and Lu(III) iodides or triflates with tris(2-pyridylmethyl)amine in rigorously anhydrous acetonitrile generates only 1:1 complexes at $n = [B]_{tot}/[M(III)]_{tot} = 1$ and only 1:2 complexes at $n = 2-4$. Hydrated 1:1 complexes of La(III), Ce(III), Nd(III), Eu(III), and Lu(III) are formed in acetonitrile in the presence of stoichiometric amounts of water at $n = 1$. Hydrated, doubly hydroxyl-bridged complexes $[MB(\mu\text{-}OH)_2MB^{4+}][OSO_2CF_3^-]_4$ are formed at $n = 2-3$.[87]

Consistent results were obtained in dry acetonitrile, showing the formation of 1:1 complexes of La(III) and U(III), when iodides react with the ligand at $n = [B]_{tot}/[M(III)]_{tot} \leq 1$. Partially dissociated 1:2 complexes are formed at $n = 1-2$ and also at $n > 2$ where no formation of 1:3 complexes is indicated. Similar results have been obtained in pyridine. The K_2 value is higher in acetonitrile than in pyridine. This is ascribed to the presence of coordinated iodide ions in the 1:1 complexes in the less polar pyridine solvent.[88]

In contrast to the above results, not only 1:1 and 1:2 but also 1:3 Eu(III) and Tb(III) complexes are reported to be formed in acetonitrile by tris(2-pyridylmethyl)amine, (*R*)- and (*S*)-[1-(2-pyridyl)ethyl]bis(2-pyridylmethyl)amine, and (*R*,*R*)- and (*R*,*S*)-bis[1-(2-pyridyl)ethyl](2-pyridylmethyl)amine.[54] It can be suspected that the formation of the 1:3 complexes was mimicked by hydrolysis of 1:1 complexes, which has undoubtedly been described more recently.[87] No information is given in ref 54 whether the experimental work was performed under strictly anhydrous conditions.

In methanol, tris(2-pyridylmethyl)amine forms a 1:1 complex with initially 0.01 M $Eu(ClO_4)_3 \cdot H_2O$ at $n = 1$. It is in equilibrium with free ligand and does not involve undissociated perchlorate ions. The Nd(III), Eu(III), and Lu(III) complexes $[MBCl_3]$ are undissociated in methanol but partially dissociate on dissolution in water under release of free ligand. Slow exchange on the NMR time scale proceeds between free ligand and the Nd(III) and Eu(III) complexes A fraction of the Lu(III) complex is converted in water, most probably to the binuclear hydroxo complex $[Lu_2B_2(OH)_2^{4+}]$.[89]

All three chelating arms of tris(2-pyridylmethyl)amine are equivalent on the NMR time scale in a 1:1 complex of Ce(III). At room temperature, the 1:1 complex displays a dynamically averaged C_{3v} structure, while a dynamically averaged D_{3h} structure is adopted by a 1:2 complex of Ce(III).[87]

All chelating ligand arms are equivalent also in the tris(2-pyridylmethyl)amine complexes $[MBCl_2^+][Cl^-]$ with M = La, Nd, Eu, Tb, and Lu, which adopt a 3-fold symmetry in methanol. The ligand is in rapid exchange between different conformations, which does not cease even at −80 °C. The discrepancy between the 1:1 electrolyte behavior of the complexes and the 3-fold symmetry is explained by exchange of the Cl^- ion between different positions, which is rapid on the NMR time scale and results in an averaged "symmetric spectrum".[89] A 3-fold symmetry, with all coordinating arms of the ligand being equivalent and possessing conformation mobility, is reported also for 1:1 complexes formed by La(III) and U(III) iodides in pyridine and acetonitrile. Complexes at 1:2 ratio adopt a dynamically averaged D_{3h} symmetry.[88]

Tris(2-benzimidazolylmethyl)amine with La(III) and U(III) iodides in pyridine forms 1:1 and 1:2 complexes at $n = [B]_{tot}/[M(III)]_{tot} = 0.5-1.5$, and only 1:2 complexes are said to be formed at $n = 2$. The ligand forms 1:2 complexes of La(III) and U(III) in pyridine more easily than tris(2-pyridylmethyl)amine.[88] It reacts in acetonitrile with La(III), Eu(III), and Lu(III) triflates under the formation of 1:1 and 1:2 complexes at $n = 1$.[90] Complexes at 1:1 ratio of La(III), Sm(III), Eu(III), and Er(III) are possibly decomplexed when dissolved in Me_2SO and MeCN, due to a strong solvent−ligand competition for the Ln^{3+} ion.[91]

Strong $\pi-\pi$ stacking of the tris(2-benzimidazolylmethyl)-amine ligand shields the central Tb^{3+} ion in the complex $[TbB_2^{3+}]$ from the solvent. The number of methanol molecules solvating the complex is as low as 0.35 ± 0.5.[90]

Complexes of La(III) and U(III) with tris(2-benzimidazolylmethyl)amine at 1:1 ratio adopt a fluxional D_{3v} symmetry in pyridine and possess a higher conformational mobility than 1:2 complexes. The 1:2 complex of La(III) is a fluxional D_{3h} symmetrical species. In a 1:2 complex of U(III), all three coordinating arms of the ligands are equivalent. The complex adopts a D_3 symmetry, the conformation of which is fixed on the NMR time scale at ≤273 K, while slow fluxional motions occur at room temperature.[88]

Complexes (1:1) formed in the reaction of La(III) and U(III) iodides with tris(2-pyrazylmethyl)amine in acetonitrile and THF adopt a C_{3v} symmetry with all three chelating arms of the ligand being equivalent. The species involve coordinated solvent molecules that exchange rapidly with bulk solvent. A complex formed in pyridine is dissociated. Tris(2-pyrazylmethyl)amine in reaction with La(III)and U(III) iodides in acetonitrile and pyridine forms only 1:1 complexes even at $n = [B]_{tot}/[M(III)]_{tot} > 2$. In pyridine, they are less stable than their tris(2-pyridylmethyl)amine analogs.[92] Lacking formation of 1:2 complexes is in contrast to tris(2-pyridylmethyl)amine, which also forms 1:2 complexes.[88]

Tris(2-pyrazylmethyl)amine reacts with $EuCl_3$ and $LuCl_3$ in methanol, but the composition of the species formed was not determined, and only an equilibrium between free ligand and its complexed form was observed. The presence of a complex that adopts a 3-fold symmetry and is in a slow exchange with ligand on the NMR time scale is indicated.[89]

Complexes resulting in the reaction of tris(2-pyrazylmethyl)amine with La(III), Nd(III), and Eu(III) perchlorates at $n = [B]_{tot}/[M(III)]_{tot} = 1$ and 298 K in acetonitrile adopt a 3-fold symmetry and undergo a fast exchange between different ligand conformations. The coordinating Cl^- counterion stabilizes the interaction of Eu(III) with the ligand, as compared with the noncoordinating ClO_4^- counterion. Eu(III) and Lu(III) complexes formed in methanol also adopt 3-fold symmetry, but the exchange with free ligand is slow on the NMR time scale. A faster exchange proceeds in methanol between La(III) and Nd(III) complexes and free ligand.[89]

A preliminary study shows that tris(2-pyridylmethyl)amine and tris(2-pyrazylmethyl)amine complexes of heavier Ln(III) are more kinetically stable than complexes of lighter Ln(III), as expected for a predominantly electrostatic interaction between the Ln^{3+} ions and the ligands. Let us remember that the 1:1 complex of Lu(III) is less thermodynamically stable than those of Nd(III) and Eu(III) (log $K_1 = 2.11$, 2.40, and 2.41 {*148,149,152*}[T3], respectively).[89]

Species produced by dissolving the complexes $[LaB(H_2O)(\eta^2\text{-}ClO_4)^{2+}][ClO_4^-]_2 \cdot 2CHCl_3 \cdot MeOH$ and $[UBI_2^+][I^-] \cdot py$ with B = tris[(2,2′-bipyridin-6-yl)methyl]amine in acetonitrile are resistant to the dissociation of the N-donor ligand. The La(III) complex species adopts a 3-fold symmetry, in which all three chelating arms of the ligand are equivalent or in fast exchange on the NMR time scale. Moreover, the arms exhibit conformation mobility. Exchange between different ligand conformations is suggested to proceed in the U(III) complex.[93]

N,*N*,*N*′,*N*′-Tetrakis(2-pyridylmethyl)-1,2-ethanediamine (B) and bis(2-ethylhexyl)phosphoric acid (HA) in 1-octanol extract Eu(III) from 0.1 M NH_4NO_3 at pH 4−5 as a complex including the cation $[EuBA_2^+]$.[94] La(III), Ce(III), and U(III) iodides form 1:1 complexes in acetonitrile at −35 to 70 °C with *N*,*N*,*N*′,*N*′-tetrakis(2-pyrazylmethyl)-1,3-propanediamine, and La(III) iodide forms a 1:1 complex with *N*,*N*,*N*′,*N*′-tetrakis(2-pyrazylmethyl)cyclohexanediamine.[95]

3.2.6. Electrolyte Behavior

Data on the electrolyte behavior of lanthanide(III) and actinide(III) complexes in organic solvents are gathered in Table 5. The dissociation mode of most complexes corresponds to the number of anions not accommodated in the coordination sphere of the M^{3+} ion. Exceptions from this rule are noted as "ex" in the last column of Table 5.

3.2.7. Theoretical Considerations

Quantum mechanics calculations were performed on terpy, TPTZ, 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine, 2,6-di(2-pyridyl)pyrazine, 2,6-di(2-benzimidazolyl)pyridine, and 2,6-bis(1,2,4-triazin-3-yl)pyridine. The calculations on free ligands indicate that in all but the last one the sum of the effective charges on the lateral rings is positive and that on the central ring is negative. The last one, 2,6-bis(1,2,4-triazin-3-yl)pyridine, has a positively charged central ring and negatively charged lateral rings. The calculations show that also in the $[EuB^{3+}]$ complexes the central ring is more positive than the lateral ones, again except 2,6-bis(1,2,4-triazin-3-yl)pyridine with a reversed charge relation. The mechanism of the complex formation of Ln(III) with planar tridentate ligands is interpreted as transfer of electronic density from the central N atom to the M^{3+} ion and the acceptance of electronic density by the lateral N atoms to form bonds with a covalence contribution.[56]

Results of the calculations delineate the main factors governing the complexation of Ln(III) by planar terdentate ligands. They are (i) degree of covalence of Ln−N bond, (ii) relation between the sizes of the nitrogen bearing cavity of the ligand and the complexed cation, (iii) the electrostatic capacity of the ligand, and (iv) the difference in the effective charges of the central and lateral N atoms.[56]

3.2.8. Kinetics of the Formation and Dissociation of the Complexes

Little is known about the kinetics of the complexation and decomplexation of Ln(III) and An(III) by N-donors in homogeneous systems. Conductometry shows that the formation of monoterpy complexes in methanolic solutions of $EuCl_3$ and $TbCl_3$ is slow at $[B]_{tot}/[M(III)]_{tot} = 1$ and room temperature, but the reaction rate has not been specified.[96]

The rate of the forward extraction of Am(III) by DPTP in TPH/1-octanol (7/3 v/v) from 0.025−2 M HNO_3 in a stirred cell is determined by a slow complexation reaction at the phase interface. The complexation is a first-order reaction with respect to the concentration of DPTP, but the observed extraction rate rate is independent of the initial nitrate concentration. Independence of the reaction rate of the NH_4NO_3 concentration at 1 M HNO_3 is a result of the compensation of two effects. Increase of the nitrate concentration accelerates the rate of the extraction, the order of which with respect to $[NO_3^-]$ is one. On the other hand, it supports the extraction of nitric acid, which decelerates the rate by lowering the concentration of free DPTP. The back extraction is controlled predominantly by diffusion, and the chemical reaction seems to play a marginal role.[19]

Several sources show time dependencies of distribution ratios in shaken test tubes, where indeed the droplet size and, thus, the interfacial area is undefined. It depends on the intensity and mode of dispersing one of the phases (manual or mechanical shaking, vortex stirrer etc.), and results from different laboratories can hardly be rigorously compared.

Out of investigated BTPs, DPTP exhibits the fastest rate of Am(III) and Eu(III) extraction. The shaking time affects only slightly the D_{Am} and D_{Eu} values in the extraction by 0.01 M DPTP in TPH/1-octanol (4/1 v/v) from 1 and 2 M HNO_3. Both D_{Am} and D_{Eu} increase a little from 4 to 10 min shaking and little change at 10−180 min shaking. D_{Am} reaches atypically a time independent value after passing a flat maximum at 10 min.[10]

Contrary to DPTP, a very slow extraction rate is exhibited by DiPTP in the absence of an organic phase modifier. No distribution equilibrium of trace Am(III) and a macro amount of Eu(III) is attained even after 60 min in the extraction by 0.01 M DiPTP in 1-octanol from 0.5 M HNO_3 + 0.0088 M light Ln(III). If trace amounts of Am(III) and Eu(III) are extracted by 0.01 M DiPTP in TPH/1-octanol (7/3) from 1 M HNO_3, the D_{Am} value passes a flat maximum at 5−10 min and becomes time

Table 5. Electrolyte Behavior of Lanthanide(III) and U(III) Complexes[a]

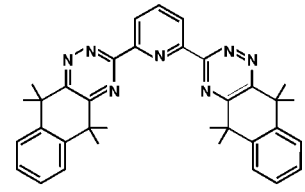
B	complex	solvent	cond., Ω^{-1} mol^{-1} cm^2	electrolyte
bipy	$[CeB_2I_2^{2+}][I^-]$	pyridine	15	1:1[59]
	0.01 M $[UB_2I_2^{2+}][I^-]$	pyridine	45	
terpy	$[LaB_3^{3+}][ClO_4^-]_3$	MeCN	364	1:3[b]
		$MeNO_2$	234	1:3[b]
	$[CeB_2I_2^{+}][I^-]$, 0.01 M $[UB_2pyI_2^{+}][I^-]$	pyridine	120	1:1[63]
	$[EuB_3^{3+}][ClO_4^-]_3$	MeCN	400	1:3[63]
		$MeNO_2$	250	1:3[63]
	$[LuB_3^{3+}][ClO_4^-]_3$	MeCN	394	1:3[63]
		$MeNO_2$	250	1:3[63]
2,6-di(2-benzimidazolyl) pyridine[c]	$[LaB_2(NO_3)_2^{+}][NO_3^-]\cdot H_2O$	MeOH	98	1:1
	$[CeB_2(NO_3)_2^{+}][NO_3^-]\cdot H_2O$	MeOH	101	1:1
	$[PrB_2(NO_3)_2^{+}][NO_3^-]\cdot H_2O$	MeOH	97	1:1
	$[NdB_2(NO_3)_2^{+}][NO_3^-]\cdot H_2O$	MeOH	94	1:1
	$[SmB_2(NO_3)_2^{+}][NO_3^-]\cdot 2H_2O$	MeOH	92	1:1
	$[EuB_2(NO_3)_2^{+}][NO_3^-]\cdot H_2O$	MeOH	86	1:1
	$[GdB_2(NO_3)_2^{+}][NO_3^-]\cdot H_2O$	MeOH	95	1:1
	$[TbB_2(NO_3)_2^{+}]$	MeOH	87	1:1
	$[DyB(B_{-H})(H_2O)(NO_3)^{+}][NO_3^-]\cdot 4H_2O$	MeOH	106	1:1
	$[ErB(B_{-H})(H_2O)(NO_3)^{+}][NO_3^-]\cdot 3H_2O$	MeOH	88	1:1
	$[Lu(B_{-H})(H_2O)(NO_3)_2]\cdot 2H_2O$	MeOH	49	weak 1:1
ligand **A** (structural formulas **2**)[77]	$[LaB(NO_3)_3]\cdot 3H_2O$	MeCN	65	non, 1:1
	$[SmB(NO_3)_3]\cdot H_2O$	MeCN	77	non, 1:1
	$[EuB(NO_3)_3]\cdot H_2O$	MeCN	85	non, 1:1
	$[GdB(NO_3)_3]\cdot H_2O$	MeCN	70	non, 1:1
	$[YbB(NO_3)_3]\cdot H_2O$	MeCN	46	non, 1:1
	$[LuB(NO_3)_3]\cdot H_2O$	MeCN	30	non, 1:1
	$[YB(NO_3)_3]\cdot H_2O$	MeCN	28	non, 1:1
TPTZ	$[EuBCl_2][Cl^-]$	MeOH	*f*	1:1[86]
	0.002 M $[EuB_3^{3+}][ClO_4^-]_3$	$MeNO_2$	173	1:3[d]
tris(2-pyridylmethyl)amine	$[LaBpyI^{2+}][I^-]_2$	MeCN	282	1:2[88]
	0.0014 M $[LaB_2^{2-}][I^-]_3$	MeCN	374	1:3[88]
	$[EuB^{3+}][ClO_4^-]_3$	MeCN	342	1:3[89]
(2-benzimidazolylmethyl)bis(2-pyridylmethyl)amine[e]	$[LaB(NO_3)_3]$	MeOH	204	1:2 (ex)
	$[EuB(NO_3)_3]$	MeOH	187	1:2 (ex)
	$[GdB(NO_3)_3]$	MeOH	219	1:2 (ex)
	$[TbB(NO_3)_3]$	MeOH	224	1:2 (ex)
	$[LaB(NO_3)_3]$, $[EuB(NO_3)_3]$, $[GdB(NO_3)_3]$, $[TbB(NO_3)_3]$	MeCN	<2	non
bis(2-benzimidazolylmethyl)-2-pyridylmethylamine (Apy = antipyrine)[e]	$[EuB(Apy)(H_2O)_2Cl^{2+}][Cl^-]_2$	MeOH	309	1:3 (ex)
	$[GdB(Apy)\ (H_2O)_2Cl^{2+}][Cl^-]_2$	MeOH	353	1:3 (ex)
	$[TbB(Apy)\ (H_2O)_2Cl^{2+}][Cl^-]_2$	MeOH	331	1:3 (ex)
	$[EuB(Apy)\ (H_2O)_2Cl^{2+}][Cl^-]_2$	MeCN	203	1:2
	$[GdB(Apy)\ (H_2O)_2Cl^{2+}][Cl^-]_2$	MeCN	185	1:2
	$[TbB(Apy)\ (H_2O)_2Cl^{2+}][Cl^-]_2$	MeCN	180	1:2

[a] Concentration = 0.001 M (if not given otherwise); T = 20−25 °C; non indicates nonelectrolyte. [b] From Durham, D. A.; Frost, G. H.; Hart, F. A. J. Inorg. Nucl. Chem. 1969, 31, 833. [c] From Wang, S.; Luo, Q.; Zhou, X.; Zeng, Z. Polyhedron 1993, 12, 1939. [d] From Durham, D. A.; Frost, G. H.; Hart, F. A. J. Inorg. Nucl. Chem. 1969, 31, 571. [e] From Yang, X.-P.; Kang, B.-S.; Wong, W.-K.k; Su, C.-Y.; Liu, H.-Q. Inorg. Chem. 2003, 42, 169. [f] Not given.

independent after 60 min, while no equilibrium D_{Eu} is attained after 120 min.[10,97] The presence of 0.5 M 2-(2-hexoxyethyl)-*N*,*N*′-dimethyl-*N*,*N*′-dioctylmalonamide as an organic phase modifier in 0.01 M DiPTP in 1-octanol accelerates the rate of the extraction from 0.5 M HNO_3 + 0.0088 M light Ln(III). An equilibrium D_{Eu} is attained in ∼30 min, while the D_{Am} passes a maximum and then slightly decreases between 15 and 60 min.[11,97]

Another BTP, namely, 0.01 M 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)-4-isononylpyridine in TPH/1-octanol (4/1 v/v) also extracts at a slow rate from 1 M HNO_3. An equilibrium D_{Am} value is attained after 60 min shaking, while the D_{Eu} value increases up to 10 min, passes a maximum at 10 min, and is time independent at >45 min. The extraction rate is similar in 1-decanol modifier but slower in the presence of lauronitrile, where time independent D_{Am} and D_{Eu} values are attained after 90 and 60 min, respectively.[10]

Monotonous time dependences of D_{Am} and D_{Eu} are observed with more recently introduced BTPs, namely, 0.01 M 2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)pyridine and 0.02 M 2,6-bis(1,3,4-triaza-9,9,10,10-tetramethyl-9,10-dihydroanthracen-2-yl)pyridine.



2,6-bis(1,3,4-triaza-9,9,10,10-tetramethyl-9,10-dihydroanthracen-2-yl)pyridine

Both have been applied in 1-octanol in the presence of the 0.5 M 2-(2-hexoxyethyl)-*N*,*N*′-dimethyl-*N*,*N*′-dioctylmalonamide modifier. Equilibrium D_{Am} and D_{Eu} values are attained in 15 min and >60 min, respectively, with the former and in 30 min with the latter.[11]

The tetradentate extractant 6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl, when applied as a 0.005 M solution in MiBK, yields time dependencies with visible maxima in the extraction of Am(III), Cm(III), and Cf(III) from 0.5 M $NaNO_3$ + 0.5 M HNO_3. The maxima are passed at a contact time of 4 min and are followed by moderate decrease of the D_M values during the whole time investigated, that is, from 4 to 60 min. Contrary to that, the D_{Eu} value continuously decreases between 1 and 60 min. In observing the whole lanthanide(III) series, the D_M values are higher after 60 min shaking than after 1 min in the extraction of Dy(III) to Lu(III). However, they are higher after 1 min than after 60 min in the extraction of La(III) to Tb(III), and the decrease of the D_M with increasing contact time can be ascribed to extrinsic effects like inconstant temperature or partial decomposition of the complexant.[84]

A similar extractant, 6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2′-bipyridyl, taken as a 0.02 M solution in 1-octanol, approaches a distribution equilibrium without passing a maximum when Am(III) and Eu(III) are extracted from 0.5 M HNO_3 + 0.0088 M light Ln(III). The equilibrium is attained after 60 min without a phase modifier and after 5 min in the presence of 0. 25−0.5 M 2-(2-hexoxyethyl)-*N*,*N*′-dimethyl-*N*,*N*′-dioctylmalonamide.[47]

It has been a step in an appropriate direction when the rate of the extraction has recently been attempted to be accelerated by phase transfer catalysts. 5,6-Dimethyl-3-(2-pyridyl)-1,2,4-triazine accelerates the extraction of Am(III) and Eu(III) by 0.05 M 6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl in TCE from 1 M HNO_3, indeed at a concentration as high as 0.8 M. In a vigorously shaken test tube, the equilibrium is attained at 20 min, compared with 60 min in the absence of a catalyst. The extraction rate is described as $D_{M,t} = (1 - e^{-At})/(D_{M,eq}{}^{-1} + e^{-At})$ and the catalyst enhances the *A* value approximately twice. 5,6,5′,6′-Tetraethyl-3,3′-bi-(1,2,4-triazinyl) is much less effective.[98]

3.2.9. Redox Reactions

The terpy/cyclopentadienyl complex cations $[MB(Cp)_2{}^+]$ (M = Ce and U) are reduced in THF by Na amalgam to the neutral species $[M(B^*)(Cp)_2]$. The reduction converts terpy to a radical form B*, while the metal retains its trivalency. The complex $[Ce(B^*)(Cp)_2]$ can be converted back to $[CeB(Cp)_2{}^+]$ by treatment with triethylammonium tetraphenylborate, in which B* is oxidized to B. Rapid and reversible charge transfer reaction between the two complexes is evidenced by ^1H NMR to occur in pyridine. Moreover, charge transfer has been observed in pyridine between complexes with different M, namely, $[CeB(Cp)_2{}^+] + [U(B^*)(Cp)_2] \leftrightarrow [Ce(B^*)(Cp)_2] + [UB(Cp)_2{}^+]$. The cationic U(III) complex is more easily reduced than the Ce(III) complex, and the concentration ratio $[CeB(Cp)_2{}^+]/[Ce(B^*)(Cp)_2] = [U(B^*)(Cp)_2]/[UB(Cp)_2{}^+]$ is 87/13.[65]

$[UB(Cp)_2{}^+]$ but not $[CeB(Cp)_2{}^+]$ reacts in pyridine readily with the $H^\bullet$ donor Ph_3SnH under the formation of the complex $[U(B')(Cp)_2{}^+]$, in which U is tetravalent and B′ is 4′-hydroterpy (i.e., 2,6-di(2-pyridyl)-1-aza-2,5-cyclohexadiene). Further hydrogenation of the ligand B′ to 2,6-di(2-pyridyl)-1-azacyclohexane requires reflux in pyridine. The cation $[U(B')(Cp)_2{}^+]$ is also formed when the neutral complex $[U(B^*)(Cp)_2]$ is treated with triethylammonium tetraphenylborate.[65]

3.3. Selective Complexation and Extraction of Actinides(III) over Lanthanides(III)

3.3.1. Selectivity in Homogenous Systems

It is seen below that U(III) has often been taken as a representative of An(III) whenever milligram or larger An(III) amounts were needed. The reason is the low α radioactivity of natural uranium, which allows laboratory work under readily realizable precautions. Am and Cm, even in trace amounts, and so much more in macro amounts, can be handled only under strict safety regulations and in an expensively equipped laboratory. The representativeness of U(III) for higher An(III) is indeed questioned in some papers.

The selectivity, a noticeable property of tridentate N-donors, is evidenced by stability constants of some Am(III) and Eu(III), as well as U(III) and Ce(III) complexes, as given in Tables 2 and 3. $K_{1(Am)}$ is higher than $K_{1(Eu)}$ in water with DMTP[24,62] {*32,39*}^{T2}, TPTZ[24,62] {*141,146*}^{T3}, and terpy[24,62] {*10,15*}^{T2}. In complexes of 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine[111] in 75−76% methanol, $K_{1(Am)}$ {*135*}^{T3} is higher than K_1 of all Ln(III) {*117−133*}^{T3} (see also Figure 4). $K_{1(U)} > K_{1(Ce)}$ and $K_{2(U)} > K_{2(Ce)}$ is valid for bipy[59] {*1,3*}^{T2} in pyridine. Contrary to purely heterocyclic ligands, ligands derived from aliphatic amines appear to be selective only in some systems. Taking tris(2-pyridylmethyl)amine[88] as one example, $K_{1(U)}$ {*153*}^{T3} in pyridine is equal to $K_{1(La)}$ {*147*}^{T3} within the experimental error. Taking tris(2-pyrazolylmethyl)amine[92] as another example, $K_{1(U)} \approx K_{1(La)}$ in pyridine {*160,161*}^{T3} but $K_{1(U)} > K_{1(La)}$ in THF {*162*}^{T3}.

The ratio $K_{1(Am)}/K_{1(Eu)}$ is 250 with DMTP, 6 with TPTZ, 4 with terpy, and 1−3 with bipy, tris(2-pyridylmethyl)amine, and tris(2-pyrazolylmethyl)amine. This corresponds to a general decrease of the selectivity in the order BTPs > terpy ≈ TPTZ > bipy ≈ pyridyl-substituted amines.

The extent of the selectivity in homogeneous solutions is further illustrated by replacement equilibria. A low selectivity is exhibited by bipy. In a solution containing CeI_3, UI_3, and bipy in pyridine at a mole ratio 1:1:1 at 21 °C, the concentration ratio of the 1:2 complex of U(III) to the 1:2 complex of Ce(III) is 4.5. With Nd(III) instead of Ce(III), the ratio is 1.7.[59]

The selectivity of terpy for U(III) over Ce(III) is also moderate. If 1 mol-equiv of terpy is added to 1 mol-equiv of each $[MI_3(py)_4]$ and $[UI_3(py)_4]$ in pyridine, the complexes $[MB_2I_2]I$ and $[UB_2(py)I_2]I$ are formed in a molar ratio of 1:3 with M = Ce and 1:2.5 with M = Nd.[63]

Essentially higher selectivity is exhibited by BTPs. If 1−3 mol-equiv of either DMTP or DPTP are added to 1 mol-equiv of each UI_3 and CeI_3 in pyridine, only the complex $[UB_3{}^{3+}]$ but not $[CeB_3{}^{3+}]$ is formed. Complexes at 1:2 and 1:3 of Ce(III) are formed only after addition of >3 mol-equiv of DMTP or DPTP. The selectivity factor was estimated as >20.[99]

DMTP also replaces terpy from lanthanide(III) and actinide(III) complexes. The terpy complex $[CeB_3{}^{3+}]$, taken as iodide or triflate, is completely converted in pyridine and acetonitrile to the DMTP analogue if 3 equiv of DMTP are added. Similarly, only the DMTP complex $[UB_3{}^{3+}][I^-]_3$ is formed from $[U(py)_4I_3]$ in the presence of 3 mol-equiv of each of terpy and DMTP in pyridine.[64]

3.3.2. Selectivity in Two-Liquid-Phase Systems

Much more data are available on heterogeneous systems involving two immiscible liquid phases, that is, on selective solvent extraction of An(III) with regard to Ln(III). The efficiency of the separation of the two groups of metals by N-donors has almost exclusively been studied with trace amounts of Am(III) and Eu(III) as representatives of the transplutonides(III) and Ln(III), respectively. The reason is the good practicability of distribution measurements, namely, the easy accessibility and radiometric determination of the isotopes ^{241}Am and ^{152,154}Eu. The most common counterion of the extracted metal ion has been 2-bromoalkanoate.

Table 6 presents a survey of data on those types of extractants, of which at least one has been reported to possess acceptable separation efficiency, that is, an $\alpha_{Am/Eu}$ value of ≥ 10. Less efficient extractants are included only if they are informative in comparison with other systems. Table 6 gives also distribution ratios of Am(III) and Eu(III), which characterize the extraction efficiency of the extractants.

Low separation efficiency ($\alpha_{Am/Eu} < 8$) is exhibited by solvents involving the following *bidentate* complexants: 2-(5,6-disubstituted-1,2,4-triazin-3-yl)pyridine + BDA in TCE with the substituent being methyl, ethyl, phenyl, 4-methoxyphenyl, 4-bromophenyl, and 2-pyridyl;[100] 2-(5,6-disubstituted-1,2,4-triazin-3-yl)-6-methylpyridine + BDA in TCE with the substituent being methyl, ethyl, phenyl, 4-methoxyphenyl, 4-bromophenyl, and 2-pyridyl;[100] 2-(5,6-disubstituted-1,2,4-triazin-3-yl)-4-*tert*-butylpyridine BDA in TCE with the substituent being methyl, ethyl, phenyl, 4-methoxyphenyl, 4-bromophenyl, and 2-pyridyl;[100] 2-(5,6-disubstituted-1,2,4-triazin-3-yl)pyrazine + BDA in TCE with the substituent being methyl, ethyl, phenyl, 4-methoxyphenyl, 4-bromophenyl, and 2-pyridyl;[100] 5,5′,6,6′-tetrasubstituted-3,3′-bitriazinyl + BDA in TCE with the substituent being methyl, ethyl, phenyl, 4-methoxyphenyl, and 4-bromophenyl;[100] 6-methyl-2-(2-quinolyl)benzimidazole in xylene/1-butanol (7/3) in the extraction from NH_4SCN.[101]

Low separation efficiency ($\alpha_{Am/Eu} < 8$) is exhibited by solvents involving the following *tridentate* complexants: 2,6-bis(5-methyl-1,3,4-oxadiazol-2-yl)pyridine and its 5-ethyl analogue, both with BDA in chlorobenzene, toluene, and TBB;[102] 2,6-bis(1-hexylbenzimidazol-2-yl)pyridine in TPH and TCE, 2-(2-benzimidazolyl)-6-(1-hexylbenzimidazol-2-yl)pyridine in TCE, 2,6-di(2-benzimidazolyl)-4-dodecoxypyridine in TCE, and 2,6-(2-benzthiazolyl)-4-dodecoxypyridine in TCE, all with BDA;[103] 2,6-bis[4,6-di(pivaloylamino)-1,3,5-triazin-2-yl]pyridine in 1-octanol, with or without BDA, in the extraction from HNO_3;[41] 4′-heptoxy-2-(2-pyrazinyl)-2,2′-bipyridyl + 1 M BDA in TPH;[104] 5,5′,6,6′-tetrasubstituted-3,3′-bitriazin-1,2,4-yl + 1 M BDA in TCE with the substituent being methyl, phenyl, 4-methoxyphenyl, 4-bromophenyl, and 2-pyridyl.[100] Data in Table 6 and in the preceding paragraphs allow some general conclusions, even if the efficiency of various ligands cannot be always compared under strictly identical conditions.

3.3.3. Effect of Extractant Structure on the Selectivity

The effect of extractant structure on the selectivity merits discussion first, because it plays an important role and has been varied more extensively than other variables. Bidentate extractants exhibit generally low separation efficiency, except 2-(2-pyridyl)benzimidazole and its methyl or chloro derivatives[101] {*3*−*7*}^{T6}, and 6-methyl-2-(1,10-phenanthrol-2-yl)-benzimidazole[101] {*8*}^{T6}. With rather rare exceptions, the bidentates also are low efficiency extractants. One exception is 5,6-dimethyl-2-(2-pyridyl)benzimidazole[101] in xylene/1-butanol {*6*}^{T6}, to be seen in comparison with other benzimidazole-type extractants {*3,4,7,8*}^{T6}. Other exceptions are 2-[5,6-di(2-pyridyl)-1,2,4-triazin-3-yl]pyridine and 2-[5,6-di(2-pyridyl)-1,2,4-triazin-3-yl]-6-methylpyridine, as compared with a group of 27 similar extractants based on 2-(5,6-substituted-1,2,4-triazin-3-yl)pyridine, 2-(5,6-substituted-1,2,4-triazin-3-yl)pyrazine, and 5,5′,6,6′-substituted-3,3′-di(1,2,4-triazinyl).[100]

Extremely high separation factors are attained in the presence of bipy or phen in the extraction by thoroughly purified bis(2,4,4-trimethylpentyl)dithiophosphonic acid[105] (Cyanex 301) {*1,2*}^{T6}. However, the efficiency cannot be ascribed to bipy and phen. They only improve the efficiency of the soft donor Cyanex 301, which, if thoroughly purified, itself yields $\alpha_{Am/Eu}$ values of several thousands.[106]

Most efficient in the Am(III)/Eu(III) separation are tri- and tetradentate ligands embodying 5,6-substituted 1,2,4-triazinyl rings attached at the 2,6-positions of a pyridine core or at the 6,6′-positions of a bipy core. The very highest separation factor, as great as 1600, is yielded by the tridentate ligand 2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)pyridine,[11,42] when it is applied together with *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-(2-hexoxyethyl)malonamide as a modifier {*33*}^{T6}. A similar ligand with a larger condensed ring, namely, 2,6-bis(9,9,10,10-tetramethyl-9,10-dihydrobenzo-1,2,4-triazaanthrane-3-yl)pyridine,[42] yields a lower but still appreciably high separation factor of 450 {*34*}^{T6}, again in the presence of the malonamide modifier. 2,6-(5,6-Dialkyl-1,2,4-triazin-3-yl)pyridines yield separation factors of 60−150 if the alkyl is methyl to n-propyl[7,8,100,104] {*27*−*30*}^{T6} or isobutyl[7] {*32*}^{T6}. To some surprise, when the alkyl is isopropyl, the separation factor is as low as 2.3 in the extraction of trace Eu(III),[8] but it is as high as 86 in the extraction of initially 0.0022 M light Ln(III), again in the presence of the malonamide modifier[97] {*31*}^{T6}. Also surprising is that 2,6-(5,6-diphenyl-1,2,4-triazin-3-yl)pyridine separates poorly {*35*}^{T6}, while its 4-methoxyphenyl, 4-bromophenyl, and 2-pyridyl analogs {*36*−*38*}^{T6} yield much higher separation factors.[100]

The tridentate ligands 6-(1,2,4-triazinyl)-substituted bipy separate Am(III) from Eu(III) with a somewhat lower but still noticeable efficiency (mostly $\alpha_{Am/Eu} = 16-30$). Of 6-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bipyridyls, the ethyl derivative {*40*}^{T6} separates better than the methyl analog {*39*}^{T6}. The separation is moderately good when alkyl is replaced by an aromatic substituent, such as phenyl {*41*}^{T6}, 4-bromophenyl {*43*}^{T6}, or 2-pyridyl {*44*}^{T6} but not 4-methoxyphenyl {*42*}^{T6}. Introduction of *tert*-butyl at the 4,4′-positions of the bipy core does not enhance the separation effectiveness of the phenyl {*45*}^{T6} and 4-bromophenyl {*46*}^{T6} derivatives.[100]

Tetradentate ditriazinyl-substituted bipy allows more efficient separation. 6,6′-Bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl[83,85] does it with $\alpha_{Am/Eu} = 60-175$ {*47*}^{T6} and 6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2′-bipyridyl[47] with $\alpha_{Am/Eu} = 100$ {*48*}^{T6}, the latter again with the *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-(2-hexoxyethyl)malonamide modifier present.

Most triazinylpyridine- and triazinylbipy-based ligands are effective extractants, especially for Am(III). They are the only N-donor extractants able to extract An(III) and Ln(III)

Table 6. Selectivity of N-Donor Extractants for Am(III) with Regard to Eu(III)[a]

no.	*N-donor extractant* (B)/organic phase composition	aqueous phase composition	D_{Am}/D_{Eu}	$\alpha_{Am/Eu}$
1	*bipy*/0.025 M B + 0.1 M purified Cyanex-301 in toluene[105]	1 M $NaNO_3$ + 0.02 M sulfanilic acid, pH 3.4	−/−	4×10^4
2	*phen*/0.01 M B + 0.1 M purified Cyanex-301 in toluene[105]	1 M $NaNO_3$ + 0.02 M sulfanilic acid, pH 3.4	−/−	4×10^4
3[43]	*2-(2-pyridyl)benzimidazole*/0.2 M B in xylene/BuOH (7/3)[101]	1 M NH_4SCN, pH 4.6 (formate buffer)	0.205/0.0125	16
4	*6-methyl-2-(2-pyridyl) benzimidazole*/0.20 M B in xylene/BuOH (7/3)[101]	1 M NH_4SCN, pH 4.2	0.67/0.025	27
	6-methyl-2-(2-pyridyl) benzimidazole/0.19 M B in xylene/BuOH (7/3)[101]	1 M NH_4SCN, pH 5.0	0.44/0.023	19
	6-methyl-2-(2-pyridyl) benzimidazole/0.19 M B in xylene/MiBK (7/3)[101]	1 M NH_4SCN, pH 5.0	2.04/0.035	58
	6-methyl-2-(2-pyridyl) benzimidazole/0.19 M B in PhCl	1 M NH_4SCN, pH 5.0	0.90/0.0172	52
5[43]	*6-methyl-2-(2-pyridyl) benzimidazole*/0.19 M B in xylene/BuOH (7/3)[101]	1 M KI	0.021/0.0046	4.4
	6-methyl-2-(2-pyridyl) benzimidazole/0.19 M B in xylene/BuOH (7/3)[101]	6.5 M $NaClO_4$	3.9/0.48	8.0
	6-methyl-2-(2-pyridyl) benzimidazole/0.31 M B + ≤0.25 M thenoic acid (HA) in xylene/BuOH (7/3)[101]	≤0.25 M NaA,	16.6/5.23	3.1
	6-methyl-2-(2-pyridyl) benzimidazole/0.29 M B in PhCl/BuOH (1/1)[101]	8.5 M $NaNO_3$ (all pH∼5)	0.39/0.060	6.6
6	*5,6-dimethyl-2-(2-pyridyl) benzimidazole*/0.28 M B in xylene/BuOH (7/3)[101]	1 M NH_4SCN, pH 5.2	7.3/0.244	30
7	*5(6)-chloro-2-(2-pyridyl) benzimidazole*/0.28 M B in xylene/BuOH (7/3)[101]	1 M NH_4SCN, pH 4−5	0.083/0.007	12
8	*6-methyl-2-(1,10-phenanthrol-2-yl) benzimidazole*/0.205 M B in xylene/1-butanol (7/3)[101]	1 M NH_4SCN, pH 5.2	0.13/0.0062	21
9	*2,6-bis(5-methyl-1,2,4-triazol-3-yl) pyridine*/0.011 M B + 1 M BHA in TPH[7]	0.05 M HNO_3 + 0.1 M NH_4NO_3	4.2/0.065	65
	2,6-bis(5-methyl-1,2,4-triazol-3-yl) pyridine/0.027 M B + 1 M BHA in TPH[7]	0.05 M HNO_3 + 0.1 M NH_4NO_3	18.5/0.31	60
	2,6-bis(5-methyl-1,2,4-triazol-3-yl) pyridine/0.026 M B + 1 M BHA in xylene/1-butanol (7/3)[7]	0.05 M HNO_3 + 0.1 M NH_4NO_3	1.34/0.075	18
10	*2,6-bis(5-butyl-1,2,4-triazol-3-yl) pyridine*/0.0138 M B + 1 M BHA in TPH[7]	0.1 M HNO_3 + 0.1 M NH_4NO_3	33/0.22	150
11	*2,6-bis(3-methyl-1,2,4-oxadiazol-5-yl)pyridine*/ 0.02 M B + 1 M BDA in PhCl[102]	HNO_3, pH 1.90	0.444/0.028	19.6
	2,6-bis(3-methyl-1,2,4-oxadiazol-5-yl) pyridine/0.02 M B + 1 M BDA in toluene[102]	HNO_3, pH 1.90	0.577/0.025	23.3
	2,6-bis(3-methyl-1,2,4-oxadiazol-5-yl) pyridine/0.02 M B + 1 M BDA in TBB[102]	HNO_3, pH 1.90	1.90/0.082	23.0
12	*2,6-bis(3-ethyl-1,2,4-oxadiazol-5-yl) pyridine*/0.02 M B + 1 M BDA in PhCl[102]	HNO_3, pH 1.90	0.012/0.0027	4.5
	2,6-bis(3-ethyl-1,2,4-oxadiazol-5-yl) pyridine/0.02 M B + 1 M BDA in toluene[102]	HNO_3, pH 1.90	0.018/0.0026	7.0
	2,6-bis(3-ethyl-1,2,4-oxadiazol-5-yl) pyridine/0.02 M B + 1 M BDA in TBB[102]	HNO_3, pH 1.90	0.076/0.0086	8.9
13	*2,6-bis(3-butyl-1,2,4-oxadiazol-5-yl) pyridine*/0.02 M B + 1 M BDA in PhCl[102]	HNO_3, pH 1.90	0.0032/ 0.0018	1.8
	2,6-bis(3-butyl-1,2,4-oxadiazol-5-yl) pyridine/0.02 M B + 1 M BDA in toluene[102]	HNO_3, pH 1.90	0.0018/ 0.0005	3.5

Table 6. Continued

no.	*N-donor extractant* (B)/organic phase composition	aqueous phase composition	D_{Am}/D_{Eu}	$\alpha_{Am/Eu}$
13	*2,6-bis(3-butyl-1,2,4-oxadiazol-5-yl) pyridine*/0.02 M B + 1 M BDA in TBB[102]	HNO_3, pH 1.90	0.0076/ 0.0023	3.3
14	*2,6-bis(5-methyl-1,2,4-oxadiazol-3-yl) pyridine*/0.02 M B + 1 M BDA in PhCl[102]	HNO_3, pH 1.90	0.333/0.0245	13.6
	2,6-bis(5-methyl-1,2,4-oxadiazol-3-yl) pyridine/0.02 M B + 1 M BDA in toluene[102]	HNO_3, pH 1.90	0.39/0.0247	15.7
	2,6-bis(5-methyl-1,2,4-oxadiazol-3-yl) pyridine/0.02 M B + 1 M BDA in TBB[102]	HNO_3, pH 1.90	1.41/0.081	17.4
15	*2,6-bis(5-ethyl-1,2,4-oxadiazol-3-yl) pyridine*/0.02 M B + 1 M BDA in PhCl[102]	HNO_3, pH 1.90	0.058/0.0055	10.5
	2,6-bis(5-ethyl-1,2,4-oxadiazol-3-yl) pyridine/0.02 M B + 1 M BDA in toluene[102]	HNO_3, pH 1.90	0.067/0.0055	12.2
	2,6-bis(5-ethyl-1,2,4-oxadiazol-3-yl) pyridine/0.02 M B + 1 M BDA in TBB[102]	HNO_3, pH 1.90	0.220/0.0154	14.3
16	*2,6-bis(5-butyl-1,2,4-oxadiazol-3-yl) pyridine*/0.02 M B + 1 M BDA in PhCl[102]	HNO_3, pH 1.90	0.040/0.0041	9.7
	2,6-bis(5-butyl-1,2,4-oxadiazol-3-yl) pyridine/0.02 M B + 1 M BDA in toluene[102]	HNO_3, pH 1.90	0.047/0.0035	13.3
	2,6-bis(5-butyl-1,2,4-oxadiazol-3-yl) pyridine/0.02 M B + 1 M BDA in TBB[102]	HNO_3, pH 1.90	0.210/0.0161	13.0
17	*2,6-bis(5-tert-butyl-1,2,4-oxadiazol-3-yl)pyridine*/ 0.02 M B + 1 M BDA in PhCl[102]	HNO_3, pH 1.90	0.0026/ 0.0017	1.5
	2,6-bis(5-tert-butyl-1,2,4-oxadiazol-3-yl)pyridine/0.02 M B + 1 M BDA in toluene[102]	HNO_3, pH 1.90	0.0015/ 0.0008	1.9
	2,6-bis(5-tert-butyl-1,2,4-oxadiazol-3-yl)pyridine/0.02 M B + 1 M BDA in TBB[102]	HNO_3, pH 1.90	0.0045/ 0.0025	1.8
18	*2,6-di(2-benzoxazolyl)-4-dodecoxypyridine*/0.04 M B + 1 M BDA in TCE[103]	0.022 M HNO_3	0.36/0.009	45
	2,6-di(2-benzoxazolyl)-4-dodecoxypyridine/0.04 M B + 1 M BDA in TCE[103]	0.042 M HNO_3	0.012/0.003	50
	2,6-di(2-benzoxazolyl)-4-dodecoxypyridine/0.04 M B + 1 M BDA in TCE[103]	0.062 M HNO_3	0.052/0.0008	60
	2,6-di(2-benzoxazolyl)-4-dodecoxypyridine/0.04 M B + 1 M BDA in TCE[103]	0.082 M HNO_3	0.029/0.0004	80
	2,6-di(2-benzoxazolyl)-4-dodecoxypyridine/0.01 M B + 1 M BDA in TBB[107]	0.01 M HNO_3	8.7/0.70	12.4
	2,6-di(2-benzoxazolyl)-4-dodecoxypyridine/0.01 M B + 1 M BDA in TBB[107]	0.01 M $HClO_4$	8.9/0.71	12.5
	2,6-di(2-benzoxazolyl)-4-dodecoxypyridine/0.01 M B + 1 M BDA in TBB[107]	0.01 M H^+ + 1 M $NaNO_3$ + 4 M $NaClO_4$	0.35/0.023	15.2
19	*2,6-di(2-benzoxazolyl)-4-(2-decyl-2-dodecylethoxy)pyridine*/0.04 M B + 1 M BDA in TCE[103]	0.021 M HNO_3	9/0.16	55
	2,6-di(2-benzoxazolyl)-4-(2-decyl-2-dodecylethoxy)pyridine/0.04 M B + 1 M BDA in TCE[103]	0.042 M HNO_3	0.7/0.017	40
	2,6-di(2-benzoxazolyl)-4-(2-decyl-2-dodecylethoxy)pyridine/0.04 M B + 1 M BDA in TCE[103]	0.061 M HNO_3	0.3/0.0054	50
	2,6-di(2-benzoxazolyl)-4-(2-decyl-2-dodecylethoxy)pyridine/0.04 M B + 1 M BDA in TCE[103]	0.081 M HNO_3	0.2/0.0031	60

Table 6. Continued

no.	*N-donor extractant* (B)/organic phase composition	aqueous phase composition	D_{Am}/D_{Eu}	$\alpha_{Am/Eu}$
19	*2,6-di(2-benzoxazolyl)-4-(2-decyl-2-dodecylethoxy)pyridine*/0.04 M B + 1 M BDA in TCE[103]	0.100 M HNO_3	0.08/0.0012	70
	2,6-di(2-benzoxazolyl)-4-(2-decyl-2-dodecylethoxy)pyridine/0.02 M B + 1 M BDA in TPH[103]	0.020 M HNO_3	11.5/0.0059	25
	2,6-di(2-benzoxazolyl)-4-(2-decyl-2-dodecylethoxy)pyridine/0.02 M B + 1 M BDA in TPH[103]	0.059 M HNO_3	0.36/0.014	30
	2,6-di(2-benzoxazolyl)-4-(2-decyl-2-dodecylethoxy)pyridine/0.02 M B + 1 M BDA in TPH[103]	0.090 M HNO_3	0.15/0.59	30
	2,6-di(2-benzoxazolyl)-4-(2-decyl-2-dodecylethoxy)pyridine/0.1 M B + 1 M BDA in TPH[103]	0.059 M HNO_3	0.51/0.017	30
	2,6-di(2-benzoxazolyl)-4-(2-decyl-2-dodecylethoxy)pyridine/0.1 M B + 1 M BDA in TPH[103]	0.083 M HNO_3	0.20/0.007	30
	2,6-di(2-benzoxazolyl)-4-(2-decyl-2-dodecylethoxy)pyridine/0.1 M B + 1 M BDA in TPH[103]	0.117 M HNO_3	0.07/0.002	35
20	*terpy*/0.02 M B + 1 M BDA in TBB[104]	0.01 M HNO_3	11.5/1.6	7.2
	terpy/0.02 M B + 1 M BDA in TPH[45]	0.03 M HNO_3	27/2.8	9.5
	terpy/0.02 M B + 1 M BDA in TPH[45]	0.05 M HNO_3	3.5/0.3	10
	terpy/0.02 M B + 1 M BDA in TPH[45]	0.08 M HNO_3	0.8/0.09	9
	terpy/0.1 M B + 1 M BDA in TBB[21]	0.04 M HNO_3	19.6/2.35	8.3
	terpy/0.1 M B + 1 M BDA in TBB[21]	0.034 M HNO_3	31.2/3.26	9.6
	terpy/0.1 M B + 1 M BDA in TBB[32]	0.036 M HNO_3	28/3.6	7.8
	terpy/0.1 M B + 1 M BDA in TBB[32]	0.08 M HNO_3	2.7/0.38	7.1
	terpy/0.1 M B + 1 M BDA in TBB[32]	0.10 M HNO_3	1.2/0.14	8.6
21	*4,4′,4″-tritert-butylterpy*/0.1 M B + 1 M BDA in TPH[32]	0.061 M HNO_3	220/18.3	12
	4,4′,4″-tritert-butylterpy/0.1 M B + 1 M BDA in TPH[32]	0.034 M HNO_3	1.12/0.098	11
22	*4′-octylterpy*/0.1 M + 1 M BDA in TPH[32]	0.005 M HNO_3	91/12.7	7.2
	4′-octylterpy/0.1 M + 1 M BDA in TPH[32]	0.034 M HNO_3	1.00/0.095	10.5
23	*4′-dodecoxyterpy*/0.02 M + 1 M BDA in TBB[104]	0.01 M HNO_3	3.7/0.49	7.6
24	*4′-(4-tolyl)-terpy*/0.02 M + 1 M BDA in TBB[104]	0.007 M HNO_3	6.6/0.78	8.5
25	*4′-(4-nitrophenyl)-terpy*/0.02 M B + 1 M BDA in TBB[104]	0.005 M HNO_3	25/2.5	10
26	*DMTP*/>0.004 M B + 1 M BDA in TCE[100]	0.013 M HNO_3	213/8.9	24
27	*DETP*/>0.004 M B + 1 M BDA in TCE[100]	0.013 M HNO_3	420/16	26
	DETP/0.0344 M B in xylene/BuOH (7/3)[7]	0.3 M HNO_3 + 1.6 M NH_4NO_3	1.36/0.0226	60
	DETP/0.0606 M B in xylene/BuOH (7/3)[b]	0.1 M HCl + 0.2 M NH_4SCN	23.5/0.16	150
	DETP/0.0606 M B in xylene/BuOH (7/3)[b]	0.1 M HCl + 0.5 M NH_4SCN	85/0.78	110
28	*DPTP*/0.0344 M B in xylene/BuOH (7/3)[7]	0.3 M HNO_3 + 1.6 M NH_4NO_3	1.66/0.023	72
	DPTP/0.0344 M B in TPH/2EhOH(4/1)[7]	0.3 M HNO_3 + 1.6 M NH_4NO_3	45.3/0.32	143
	DPTP/0.0344 M B in TPH/2EhOH(4/1)[7]	0.5 M HNO_3 + 1.4 M NH_4NO_3	33.1/0.26	128
	DPTP/0.0344 M B in TPH/2EhOH(4/1)[7]	0.9 M HNO_3 + 1.0 M NH_4NO_3	22.6/0.17	131
	DPTP/0.0286 M B in TPH/2EhOH(4/1)[8]	0.1 M HNO_3 + 1.0 M NH_4NO_3	20.0/0.16	125
	DPTP/0.0286 M B in TPH/2EhOH(4/1)[8]	0.1 M HNO_3 + 5.0 M NH_4NO_3	300/2.3	130
29	*DPTP*/0.011 M B in TPH/2EhOH (4/1)[8]	0.3 M HNO_3 + 1.6 M NH_4NO_3	3.67/0.032	113
	DPTP/0.011 M B in cyc-C_6H_{12}/2EhOH[8] (4/1)		1.41/0.015	96
	DPTP/0.011 M B in MiBK/2EhOH (4/1)[8]		0.857/0.015	56
	DPTP/0.011 M B in 2-Eh acet/2EhOH (4/1)[8]		0.293/0.0048	61
	DPTP/0.011 M B in benzene/2-EhOH (4/1)[8]		0.237/0.0056	42
	DPTP/0.011 M B in chlorobenzene/2EhOH (4/1)[8]		0.152/0.0038	40
	DPTP/0.011 M B in xylene/2EhOH (4/1)[8]		0.083/0.0023	36
	DPTP/0.0295 M B in xylene/BuOH (7/3)[8]		1.66/0.0230	72
30	*DPTP*/0.011 M B in TPH/BuOH (6.6/1)[8]	0.3 M HNO_3 + 1.6 M NH_4NO_3	17.3/0.26	67

Table 6. Continued

no.	*N-donor extractant* (B)/organic phase composition	aqueous phase composition	D_{Am}/D_{Eu}	$\alpha_{Am/Eu}$
30	*DPTP*/0.011 M B in TPH/BuOH (3.7/1)[8]	0.3 M HNO_3 + 1.6 M NH_4NO_3	22.7/0.195	116
	DPTP/0.011 M B in TPH/BuOH (1.2/1)[8]	0.3 M HNO_3 + 1.6 M NH_4NO_3	5.23/0.046	113
	DPTP/0.011 M B in TPH/1-octanol (19/1)[8]	0.3 M HNO_3 + 1.6 M NH_4NO_3	4.23/0.043	98
	DPTP/0.011 M B in TPH/1-octanol (3.7/1)[8]	0.3 M HNO_3 + 1.6 M NH_4NO_3	4.68/0.041	115
	DPTP/0.011 M B in TPH/1-octanol (1.2/1[8]	0.3 M HNO_3 + 1.6 M NH_4NO_3	1.64/0.020	82
	DPTP/0.011 M B in TPH/2EhOH (19/1)[8]	0.3 M HNO_3 + 1.6 M NH_4NO_3	2.94/0.032	92
	DPTP/0.011 M B in TPH/2EhOH (3.7/1)[8]	0.3 M HNO_3 + 1.6 M NH_4NO_3	4.32/0.037	116
	DPTP/0.011 M B in TPH/2EhOH (1.2/1)[8]	0.3 M HNO_3 + 1.6 M NH_4NO_3	2.28/0.020	112
31	*DiPTP*/0.022 M B in TPH/2EhOH (4/1)[8]	0.3 M HNO_3 + 1.6 M NH_4NO_3	86/39	2.3
	DiPTP/0.01 M B in 1-octanol[97]	1.0 M HNO_3	19.8/4.1	4.8
	DiPTP/0.01 M B + 0.5 M *N,N′*-dimethyl-*N,N′*-dioctyl-2-(2-hexoxyethyl)-malonamide in 1-octanol[97]	0.5 M HNO_3 + 0.0022 M total light Ln(III)	8.6/0.1	86
32	*DiBTP*/0.0286 M B in TPH/2EhOH (4/1)[7]	0.9 M HNO_3 + 1.0 M NH_4NO_3	72/0.54	132
33	*2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)pyridine*/0.01 M B + 0.5 M *N,N′*-dimethyl-*N,N′*-dioctyl-2-(2-hexoxyethyl)-malonamide in 1-octanol[11,42]	0.5 M HNO_3 + 0.0088 M total light Ln(III)	500/0.31	1600
34	*2,6-bis(9,9,10,10-tetramethyl-9,10-dihydrobenzo-1,2,4-triazaanthrane-3-yl)pyridine*/0.02 M B in 1-octanol[42]	0.5 M HNO_3 + 0.0088 M total light Ln(III)	0.50/0.0032	160
	2,6-bis(9,9,10,10-tetramethyl-9,10-dihydrobenzo-1,2,4-triazaanthrane-3-yl)pyridine/0.02 M B + 0.5 M *N,N′*-dimethyl-*N,N′*-dioctyl-2-(2-hexoxyethyl)-malonamide in 1-octanol[42]	0.5 M HNO_3 + 0.0088 M total light Ln(III)	12.6/0.028	450
35	*2,6-bis(5,6-diphenyl-1,2,4-triazin-3-yl) pyridine*/>0.004 M B + 1 M BDA in TCE[100]	0.032 M HNO_3	<1000/<210	4.8
36	*2,6-bis[5,6-di(4-methoxyphenyl)-1,2,4-triazin-3-yl]pyridine*/>0.004 M B + 1 M BDA in TCE[100]	0.032 M HNO_3	<1000/<20	(50)
37	*2,6-bis[5,6-di(4-bromophenyl)-1,2,4-triazin-3-yl]pyridine*/>0.004 M B + 1 M BDA in TCE[100]	0.013 M HNO_3	264/10	26
38	*2,6-bis[5,6-di(2-pyridyl)-1,2,4-triazin-3-yl]pyridine*//>0.004 M B + 1 M BDA in TCE[100]	0.013 M HNO_3	34/1.9	18
39	*6-(5,6-dimethyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl*/>0.004 M B + 1 M BDA in TCE[100]	0.013 M HNO_3	9.4/0.59	16
40	*6-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl*/>0.004 M B + 1 M BDA in TCE[100]	0.013 M HNO_3	92/3.1	30
	6-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl/0.02 M B+ 1 M BDA in TPH[43]	0.021 M HNO_3	20.2/1.2	17
	6-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl/0.02 M B+ 1 M BDA in TPH	0.060 M HNO_3	0.5/0.029	19
	6-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl/0.1 M B + 1 M BDA in TPH[43]	0.021 M HNO_3	102/3.9	26
	6-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl/0.1 M B + 1 M BDA in TPH	0.060 M HNO_3	3.9/0.13	30
41	*6-(5,6-diphenyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl*/>0.004 M B + 1 M BDA in TCE[100]	0.013 M HNO_3	10.2/0.39	26

Table 6. Continued

no.	*N-donor extractant* (B)/organic phase composition	aqueous phase composition	D_{Am}/D_{Eu}	$\alpha_{Am/Eu}$
42	*6-[5,6-di-(4-methoxyphenyl)-1,2,4-triazin-3-yl]-2,2′-bipyridyl/*>0.004 M B + 1 M BDA in TCE[100]	0.013 M HNO_3	26/2.9	9.0
43	*6-[5,6-di-(4-bromophenyl)-1,2,4-triazin-3-yl]-2,2′-bipyridyl/*>0.004 M B + 1 M BDA in TCE[100]	0.013 M HNO_3	26/1.00	26
44	*6-[5,6-di-(2-pyridyl)-1,2,4-triazin-3-yl]-2,2′-bipyridyl/*>0.004 M B + 1 M BDA in TCE[100]	0.013 M HNO_3	5.6/0.40	14
45	*6-(5,6-diphenyl-1,2,4-triazin-3-yl)-4,4′-ditert-butyl-2,2′-bipyridyl/*>0.004 M B + 1 M BDA in TCE[100]	0.013 M HNO_3	8.0/0.28	29
46	*6-[5,6-di-(4-bromophenyl)-1,2,4-triazin-3-yl]-4,4′-ditert-butyl-2,2′-bipyridyl/*>0.004 M B + 1 M BDA in TCE[100]	0.013 M HNO_3	1.1/0.085	13
47	*6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl*/0.015 M B in kerosene/1-octanol (7/3v/v)[83]	1.0 M HNO_3	3.86/0.022	175
	6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl/0.01 M B + 0.5 M BHA in TBB[83]	1.0 M HNO_3	4.43/0.075	60
	6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl/0.01 M B + 0.5 M BDA in TBB[85]	0.01 M HNO_3 + 0.99 M $NaNO_3$	620/4	155
	6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl/0.005 M B in nitrobenzene[85]	0.01 M HNO_3 + 0.99 M $NaNO_3$	950/6.7	140
	6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl/0.005 M B in cyclohexanone[85]	0.01 M HNO_3 + 0.99 M $NaNO_3$	36/0.46	80
	6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl/0.005 M B in TCE[85]	0.01 M HNO_3 + 0.99 M $NaNO_3$	1.5/0.014	110
	6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl/0.005 M B in 1-decanol[85]	0.01 M HNO_3 + 0.99 M $NaNO_3$	0.046/0.0044	10
48	*6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2′-bipyridyl*/0.01 M B + *N,N′*-dimethyl-*N,N′*-dioctyl-2-(2-hexoxyethyl) malonamide in 1-octanol[47]	0.02 M HNO_3 + 0.5 M NH_4NO_3	2.65/0.028	100
49	*2-amino-4,6-di(2-pyridyl)-1,3,5-triazine*/0.02 M B + 1 M BDA in TPH[45]	0.03 M HNO_3	45/4.6	9.5
	2-amino-4,6-di(2-pyridyl)-1,3,5-triazine/0.02 M B + 1 M BDA in TPH[45]	0.05 M HNO_3	5.5/0.5	10
	2-amino-4,6-di(2-pyridyl)-1,3,5-triazine/0.02 M B + 1 M BDA in TPH[45]	0.08 M HNO_3	0.7/0.08	9.5
50	*2-(octanoylamino)-4,6-di(2-pyridyl)-1,3,5-triazine*/0.02 M B + 1 M BDA in TPH[45]	0.03 M HNO_3	19/2.4	8
	2-(octanoylamino)-4,6-di(2-pyridyl)-1,3,5-triazine/0.02 M B + 1 M BDA in TPH[45]	0.06 M HNO_3	3.5/0.3	12
	2-(octanoylamino)-4,6-di(2-pyridyl)-1,3,5-triazine/0.02 M B + 1 M BDA in TPH[45]	0.10 M HNO_3	0.4/0.03	12
51	*2-(3,3,5-trimethylhexanoylamino)-4,6-di(2-pyridyl)-1,3,5-triazine*/0.02 M B + 1 M BDA in TPH[45]	0.02 M HNO_3	14/2.2	6.5
	2-(3,3,5-trimethylhexanoylamino)-4,6-di(2-pyridyl)-1,3,5-triazine/0.02 M B + 1 M BDA in TPH[45]	0.04 M HNO_3	4.8/0.5	9.5
	2-(3,3,5-trimethylhexanoylamino)-4,6-di(2-pyridyl)-1,3,5-triazine/0.02 M B + 1 M BDA in TPH[45]	0.06 M HNO_3	1.1/0.12	9
52	*2-(cyclohexanoylamino)-4,6-di(2-pyridyl)-1,3,5-triazine*/0.02 M B + 1 M BDA in TPH[45]	0.03 M HNO_3	24/2.2	11

Table 6. Continued

no.	*N-donor extractant* (B)/organic phase composition	aqueous phase composition	D_{Am}/D_{Eu}	$\alpha_{Am/Eu}$
52	*2-(cyclohexanoylamino)-4,6-di(2-pyridyl)-1,3,5-triazine*/0.02 M B + 1 M BDA in TPH[45]	0.05 M HNO_3	2.8/0.24	12
	2-(cyclohexanoylamino)-4,6-di(2-pyridyl)-1,3,5-triazine/0.02 M B + 1 M BDA in TPH[45]	0.10 M HNO_3	0.4/0.04	10
53	*TPTZ*/0.02 M + 1 M BDA in TPH[32]	0.028 M HNO_3	26/2.8	9.3
	TPTZ/0.02 M + 1 M BDA in TPH[32]	0.053 M HNO_3	3.4/0.30	11.3
	TPTZ/0.02 M + 1 M BDA in TPH[32]	0.078 M HNO_3	0.82/0.083	9.9
	TPTZ/0.1 M B + 1 M BDA in TBB[21]	0.05 M HNO_3	2.8/0.28	10.0
	TPTZ/0.01 M B + 1 M BDA in decanol[5,6]	1 M KNO_3, pH 2.82	0.38/0.053	7.2
	TPTZ/0.01 M B + 1 M BDA in decanol[5,6]	1 M KNO_3, pH 2.67	0.16/0.017	9.4
	TPTZ/0.01 M B + 0.01 M DNNS in TBB[5,6]	0.08 M HNO_3	1.35/0.20	6.8
	TPTZ/0.01 M B + 0.01 M DNNS in TBB[5,6]	0.12 M HNO_3	6.30/0.50	12.6
54	erroneously assigned to *TPTZ*, valid for *2,4,6-tris(4-tert-butylpyrid-2-yl)-1,3,5-triazine*, see row 55/0.02 M B + 1 M BDA in TPH[45]	0.03 M HNO_3	124/8.7	14.2
	erroneously assigned to *TPTZ*, valid for *2,4,6-tris(4-tert-butylpyrid-2-yl)-1,3,5-triazine*, see row 55/0.02 M B + 1 M BDA in TPH[45]	0.05 M HNO_3	12/0.9	13.3
	erroneously assigned to *TPTZ*, valid for *2,4,6-tris(4-tert-butylpyrid-2-yl)-1,3,5-triazine*, see row 55/0.02 M B + 1 M BDA in TPH[45]	0.08 M HNO_3	2.1/0.2	10.5
55	*2,4,6-tris(4-tert-butylpyrid-2-yl)-1,3,5-triazine*/0.02 M B + 1 M BDA in TPH[32]	0.03 M HNO_3	124/8.7	14.2
	2,4,6-tris(4-tert-butylpyrid-2-yl)-1,3,5-triazine/0.02 M B + 1 M BDA in TPH[32]	0.05 M HNO_3	12/0.9	13.3
	2,4,6-tris(4-tert-butylpyrid-2-yl)-1,3,5-triazine/0.02 M B + 1 M BDA in TPH[32]	0.08 M HNO_3	2.1/0.2	10.5
56	*tris(2-pyridylmethyl)amine*/0.001 M B + 1 M BDA in TPH[89]	0.012 M HNO_3	0.25/0.13	1.9
	tris(2-pyridylmethyl)amine/0.001 M B + 1 M BDA in TPH[89]	0.014 M HNO_3	0.22/0.12	1.8
57	*tris(2-pyrazylmethyl)amine*/0.001 M B + 1 M BDA in TPH[89]	0.011 M HNO_3	0.46/0.13	3.5
	tris(2-pyrazylmethyl)amine/0.001 M B + 1 M BDA in TPH[89]	0.013 M HNO_3	0.44/0.16	2.7
	tris(2-pyrazylmethyl)amine/0.02 M B + 1 M BDA in TPH[89]	0.009 M HNO_3	4.60/0.43	10.8
	tris(2-pyrazylmethyl)amine/0.02 M B + 1 M BDA in TPH[89]	0.06 M HNO_3	0.004/0.0004	10
	tris(2-pyrazylmethyl)amine/0.1 M B + 1 M BDA in TPH[109]	0.06 M HNO_3	0.2/0.008	25
58	*N,N,N′,N′-tetrakis(2-pyridyl- methyl)-1,2-ethanediamine*/0.001 M B in 1-octanol[108]	0.1 M NH_4NO_3, pH 4.6	0.010/ 0.00043	23
	N,N,N′,N′-tetrakis(2-pyridyl- methyl)-1,2-ethanediamine/0.001 M B in nitrobenzene[108]	0.1 M NH_4NO_3, pH 4.16	2.0/0.0099	200
	N,N,N′,N′-tetrakis(2-pyridyl- methyl)-1,2-ethanediamine/0.001 M B in nitrobenzene[108]	0.1 M NH_4NO_3, pH 5.15	15/0.33	45
	N,N,N′,N′-tetrakis(2-pyridyl- methyl)-1,2-ethanediamine/0.001 M B + 0.1 M octanoic acid in 1-octanol[c]	0.1 M NH_4NO_3, pH 4.8	2.7/0.022	123
	N,N,N′,N′-tetrakis(2-pyridyl- methyl)-1,2-ethanediamine/0.01 M B + 0.02 M decanoic acid in 1-octanol[c]	0.1 M NH_4NO_3, pH 4.7	1.15/0.014	84
	N,N,N′,N′-tetrakis(2-pyridyl- methyl)-1,2-ethanediamine/0.00174 M B + 0.004 M bis(2- ethylhexyl) phosphoric acid in 1- octanol[94]	0.1 M NH_4NO_3, pH 4.3	86/1.2	72

Table 6. Continued

no.	*N-donor extractant* (B)/organic phase composition	aqueous phase composition	D_{Am}/D_{Eu}	$\alpha_{Am/Eu}$
58	*N,N,N′,N′-tetrakis(2-pyridyl- methyl)-1,2-ethanediamine*/0.002 M B + 0.004 M bis(2-ethylhexyl) phosphoric acid in do decane/1-octanol (7/3 v/v)[94]	0.1 M NH_4NO_3, pH 4.2	107/8.2	13.0
59	*N,N,N′,N′-tetrakis(2-pyridyl-methyl)-5,6-decanediamine*/0.01 M B in nitrobenzene[108]	3.0 M NH_4NO_3, pH 4.1	0.008/0.0007	11
	N,N,N′,N′-tetrakis(2-pyridyl-methyl)-5,6-decanediamine/0.01 M B in nitrobenzene[124]	3.0 M NH_4NO_3, pH 5.1	0.089/0.0026	34
60	*N,N,N′,N′-tetrakis(2-pyridylmethyl)-trans-1,2-diaminocyclohexane*[108]/0.001 M B in 1-octanol[108]	0.1 M NH_4NO_3, pH 4.64	0.0017/ 0.0007	2.4
	N,N,N′,N′-tetrakis(2-pyridylmethyl)-trans-1,2-diaminocyclohexane[108]/0.001 M B in 1-octanol[124]	0.1 M NH_4NO_3, pH 5.63	0.022/0.0061	3.6
61	*N,N,N′,N′-tetrakis(2-pyridylmethyl)-cis-1,2-diaminocyclohexane*/0.001 M B in 1-octanol[108]	0.1 M NH_4NO_3, pH 4.75	0.0043/ 0.0024	1.8
62	*N,N,N′,N′-tetrakis(2-pyrazylmethyl)-1,2-ethanediamine*[109]/0.02 M B + 1 M BDA in TPH[109]	0.06 M HNO_3	0.02/0.0005	40
	N,N,N′,N′-tetrakis(2-pyrazylmethyl)-1,2-ethanediamine[109]/0.1 M B + 1 M BDA in TPH[109]	0.03 M HNO_3	45/0.6	75
	N,N,N′,N′-tetrakis(2-pyrazylmethyl)-1,2-ethanediamine[109]/0.1 M B + 1 M BDA in TPH[109]	0.06 M HNO_3	0.5/0.007	70
63	*N,N,N′,N′-tetrakis(2-pyrazylmethyl)-1,3-propanediamine*/0.08 M B + 1 M BDA in TPH[109]	0.04 M HNO_3	1.1/0.5	2.2
	N,N,N′,N′-tetrakis(2-pyrazylmethyl)-1,3-propanediamine/0.2 M B + 1 M BDA in TPH[109]	0.06 M HNO_3	0.2/0.1	2.3
	N,N,N′,N′-tetrakis(2-pyrazylmethyl)-1,3-propanediamine/0.2 M B + 1 M BDA in TPH[109]	0.06 M HNO_3	79/54	1.5
64	*N,N,N′,N′-tetrakis(2-pyrazylmethyl)-trans-1,2-diaminocyclohexane*/0.02 M B + 1 M BDA in TPH[109]	0.04 M HNO_3	0.004/0.002	2
	N,N,N′,N′-tetrakis(2-pyrazylmethyl)-trans-1,2-diaminocyclohexane/0.05 M B + 1 M BDA in TPH[109]	0.02 M HNO_3	0.04/0.02	2

[a] Trace amounts, if not indicated otherwise. BHA = 2-bromohexanoic acid; BDA = 1 M 2-bromodecanoic acid; Cyanex 301 = bis(2,4,4-trimethylpentyl)dithiophosphonic acid; TBB = *tert*-butylbenzene; TCE = 1,1,2,2-tetrachloroethane; ng = not given. [b] From Kolarik, Z.; Müllich, U.; Gassner, F. German Patent 198 10 895 1998; Chem. Abstr. 1999, 131, 343397. [c] From Mirvaliev, R.; Watanabe, M.; Matsumura, T.; Tachimori, S.; Takeshita, K. J. Nucl. Sci. Tecnol. 2004, 41, 1122.

as nitrates. Further development of these extractants is directed to the enhancement of their chemical and radiolytic stability in nitric acid media, which is not satisfactory at >1 M HNO_3 (see section 2.7). It should be noticed that improvement of the chemical stability may be counterbalanced by a deterioration of the extraction rate, which anyway becomes slower at increasing alkyl size and branching. For example, distribution equilibrium is attained after 2−4 min shaking with DPTP, but after ≥3 h with the more stable DiBTP extractant.[7]

High separation factors are also achieved with side-ring substituted 2,6-ditriazolylpyridines. As well as other extractants discussed below, they are not able to extract An(III) and Ln(III) as nitrates and can be applied with a good effectiveness in the extraction of 2-bromoalkanoates. The $\alpha_{Am/Eu}$ values attained with 2,6-bis(5-methyl-1,2,4-triazol-3-yl)pyridine $\{9\}^{T6}$ and 2,6-bis(5-butyl-1,2,4-triazol-3-yl)pyridine $\{10\}^{T6}$ are 61 and 150, respectively.[7]

Less effective are 2,6-dioxazolylpyridines, of which only 2,6-bis(3-methyl-1,2,4-oxadiazol-5-yl)pyridine $\{11\}^{T6}$ and 2,6-bis(5-methyl-1,2,4-oxadiazol-3-yl)pyridine $\{14\}^{T6}$ combine appropriate separation and extraction efficiency, giving $\alpha_{Am/Eu}$ values of 23 and 17.4, respectively. 2,6-Bis(5-ethyl-1,2,4-oxadiazol-3-yl)pyridine $\{15\}^{T6}$ and 2,6-bis(5-butyl-1,2,4-oxadiazol-3-yl)pyridine $\{16\}^{T6}$ separate rather well ($\alpha_{Am/Eu}$ = 14.3 and 13.0, respectively), but they are very weak extractants. Generally, both the separation and extraction efficiency deteriorate with the alkyl size at the same position of the oxadiazol ring, for example, in the alkyl order methyl > ethyl > butyl in 2,6-bis(3-alkyl-1,2,4-oxadiazol-5-yl)pyridines $\{11-13\}^{T6}$ and methyl > ethyl > butyl > *tert*-butyl in 2,6-bis(5-alkyl-1,2,4-oxadiazol-3-yl)pyridines $\{14-17\}^{T6}$. Finally, the effect of the isomerism of the oxadiazol ring is nonuniform and is illustrated by the efficiencies decreasing in the sequences 2,6-bis(3-methyl-1,2,4-oxadiazol-5-yl)pyridine $\{11\}^{T6}$ > 2,6-bis(5-methyl-1,3,4-oxadiazol-3-yl)pyridine $\{14\}^{T6}$ > 2,6-bis(5-methyl-1,3,4-oxadiazol-2-yl)pyridine[102] and 2,6-bis(5-ethyl-1,3,4-oxadiazol-3-yl)pyridine $\{15\}^{T6}$ > 2,6-bis(3-ethyl-1,2,4-oxadiazol-5-yl)pyridine $\{12\}^{T6}$ > 2,6-bis(5-ethyl-1,3,4-oxadiazol-2-yl)pyridine.[102]

While the separation and extraction efficiency of N-substituted 2,6-di(benzimidazolyl)pyridines and a substituted di(benzthiazolyl)pyridine[103] is low, 4-substituted 2,6-di(benzoxazolyl)pyridines are more efficient. The separation efficiency is higher with the 4-substituent being 2-decyl-2-dodecylethoxyl[103] {*18*}^{T6} than with dodecoxyl[107] {*19*}^{T6}.

Terpy separates with a moderate efficiency,[21,32,45,104] yielding $\alpha_{Am/Eu}$ values of 7−10 {*20*}^{T6}. The efficiency is not influenced by introduction of lipophilic substituents at the 4′-position, namely of octyl[32] {*22*}^{T6}, dodecoxyl[104] {*23*}^{T6}, *p*-tolyl[104] {*24*}^{T6}, and 4-nitrophenyl[104] {*25*}^{T6}. Slightly higher $\alpha_{Am/Eu}$ value (11.4) is attained with 4,4′,4″-tri-*tert*-butyl terpy[32] {*21*}^{T6}, where enhancement of the lipophilic character has been the initial purpose of the substitution. In contrast to the separation efficiency, the effectiveness of the extraction by terpy is strongly influenced by the substitution. It decreases in the order terpy[21,32,45,104] {*20*}^{T6} > 4,4′,4″-tri-*tert*-butylterpy[32] {*21*}^{T6} > 4′-octylterpy[32] {*22*}^{T6} and terpy[21,32,45,104] {*20*}^{T6} > 4′-(p-tolyl)terpy[104] {*24*}^{T6} > dodecoxyterpy[104] {*23*}^{T6}.

Much attention has been paid to 2,4,6-derivatives of 1,3,5-triazine, of which TPTZ was the first N-donor recognized to extract Am(III) selectively over Eu(III).[5] The $\alpha_{Am/Eu}$ value ranges from 9 to 14[5,6,21,32] and is thus slightly higher than that in the extraction by terpy and its derivatives. In a series of 2-amino-substituted 4,6-di(2-pyridyl)-1,3,5-triazines,[45] the separation efficiency decreases in the substituent order amino {*49*}^{T6} > 2-octanoylamino {*50*}^{T6} ≈ 2-cyclohexanoylamino {*52*}^{T6} > 3,5,5-trimethylhexanoylamino {*51*}^{T6}. The more lipophilic ligand 2,4,6-tris(4-*tert*-butylpyrid-2-yl)-1,3,5-triazine[32] separates similarly to TPTZ, giving $\alpha_{Am/Eu}$ = 10.5−14.2 {*55*}^{T6}, but it exhibits a higher extraction efficiency. It has to be noticed that data given in row {*54*}^{T6} were obtained with 2,4,6-tris(4-*tert*-butylpyrid-2-yl)-1,3,5-triazine, but in the original source,[45] they were erroneously ascribed to TPTZ (cf. {*55*}^{T6}).

The tetradentate ligands tris(2-pyridylmethyl)amine {*56*}^{T6} and tris(2-pyrazylmethyl)amine {*57*}^{T6} are at their concentrations of 0.001 M little effective in the separation ($\alpha_{Am/Eu}$ = 1.8−3.5) and also in the extraction. However, the latter surprisingly exhibits an enhanced separation efficiency at higher concentration,[89] yielding an $\alpha_{Am/Eu}$ of 10 at 0.02 M and 23 at 0.1 M {*57*}^{T6}. Hexadentate alkanediamine ligands change their extractant properties to a surprising extent with the length and substitution of the -$(CH_2)_n$- bridge. So *N*,*N*,*N*′,*N*′-tetrakis(2-pyrazylmethyl)-1,2-ethanediamine[109] yields separation factors as high as 35 at 0.02 M and 70−75 at 0.1 M {*62*}^{T6}, while an $\alpha_{Am/Eu}$ value of merely 1.5−2.3 is attained with its propane analogue *N*,*N*,*N*′,*N*′-tetrakis(2-pyrazylmethyl)-1,2-propanediamine[109] at 0.2 M {*63*}^{T6}. Similarly, *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-5,6-decanediamine[108] {*59*}^{T6} separates much less efficiently than *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethanediamine[108] {*58*}^{T6}.

The alicyclic analogs *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-*trans*-1,2-diaminocyclohexane[108] {*60*}^{T6}, *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-*cis*-1,2-diaminocyclohexane[108] {*61*}^{T6}, and *N*,*N*,*N*′,*N*′-tetrakis(2-pyrazylmethyl)-*trans*-1,2-diaminocyclohexane[109] {*64*}^{T6} yield $\alpha_{Am/Eu}$ values as low as ∼2. The dissimilarities between the separation efficiency are ascribed not to steric factors but to a difference in the conformations preferred by the hexadentate ligands due to different ligand architecture.[109]

3.3.4. Effect of Diluent and Phase Modifier on the Selectivity

The diluent can influence the Am(III)/Eu(III) separation quite noticeably. It is indeed true that the efficiency of the extraction of Am(III) and Eu(III) mostly changes concurrently with varying diluent nature, but the extent of the change is different. The separation and extraction efficiency of the bidentate extractant 6-methyl-2-(2-pyridyl)benzimidazole {*4*}^{T6} decreases in the diluent order xylene/MiBK > chlorobenzene > xylene/1-butanol.[101] The separation efficiency of 2,6-bis(3-alkyl-1,2,4-oxadiazol-5-yl)pyridines {*11,12,13*}^{T6} changes in the diluent order *tert*-butylbenzene ≈ toluene > chlorobenzene. The separation by 2,6-bis(5-alkyl-1,2,4-oxadiazol-3-yl)pyridine follows the same order if alkyl = butyl {*16*}^{T6} and *tert*-butyl {*17*}^{T6}. However, if alkyl = methyl {*14*}^{T6} and ethyl {*15*}^{T6}, the order is *tert*-butylbenzene > toluene >chlorobenzene.[102] 2,6-Bis(5-methyl-1,2,4-triazol-3-yl)pyridine[7] yields an essentially higher $\alpha_{Am/Eu}$ value in TPH than in xylene/1-octanol (7/3) {*9*}^{T6}.

The effectiveness of the separation and extraction by DPTP in 4/1 (v/v) mixtures of diluent and 2-ethyl-1-hexanol varies in the sequence TPH > cyclohexane > MiBK > 2-ethylhexyl acetate > benzene > chlorobenzene > xylene {*29*}^{T6}. The $\alpha_{Am/Eu}$ value decreases in this sequence from 113 to 36. The alcohol is added as a phase modifier enhancing the solubility of DPTP. When the volume fraction of an alcohol is varied in a broad range in mixtures with TPH, the separation and extraction efficiency of DPTP changes nonmonotonously and passes a flat maximum at a TPH/alcohol ratio of 3.7 {*30*}^{T6}. A maximum $\alpha_{Am/Eu}$ value of 116 is attained when the alcohol is 1-butanol, 1-octanol, and 2-ethyl-1-hexanol, that is, without any effect of the chain length and branching of the alcohol molecule. The extraction efficiency is at its highest with 1-butanol, but it is little affected by branching of the octanols.[8]

An example of the effect of a phase modifier other than an alcohol is the extraction by 2,6-bis(9,9,10,10-tetramethyl-9,10-dihydrobenzo-1,2,4-triazaanthrane-3-yl)pyridine. In this system *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-(2-hexoxyethyl)malonamide is the phase modifier and 1-octanol is the diluent. The $\alpha_{Am/Eu}$ value is suppressed from 450 in the presence of the modifier to 160 in its absence {*34*}^{T6}, and also the extraction efficiency is deteriorated.[42]

The separation efficiency of the tetradentate extractant 6,6′-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl decreases in the order nitrobenzene > tetrachloroethane > cyclohexanone >1-decanol. The extraction efficiency decreases steeply in a different sequence, namely, nitrobenzene > cyclohexanone > tetrachloroethane >1-decanol[85] {*47*}^{T6}.

The effect of the diluent polarity is not uniform. The separation efficiency is higher in a less polar diluent in the extraction by 2,6-bis(5-methyl-1,2,4-triazol-3-yl)pyridine[7] {*9*}^{T6} (TPH > xylene/1-butanol (7/3)) and TPTZ[5,6] {*53*}^{T6} (tri-*tert*-butylbenzene > decanol). On the other hand, $\alpha_{Am/Eu}$ is higher in a more polar diluent in the extraction by 2,6-di(2-benzoxazolyl)-4-dodecoxypyridine[103,107] {*18*}^{T6} and 2,6-di(2-benzoxazolyl)-4-(2-decyl-2-dodecylethoxy)pyridine[103] {*19*}^{T6} (tetrachloroethane > TPH or TBB). Also the synergistic mixture *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethanediamine + bis(2-ethylhexyl)phosphoric acid[94] {*58*}^{T6} separates better in a more polar diluent (1-octanol > TPH/1-octanol (7/3)).

Table 7. Separation of Am(III) from Other Metals M[a]

		$\alpha_{Am/M}$ at 0.1 M HNO_3 + var. $NaNO_3$				$\alpha_{Am/M}$ at var. HNO_3		
system	M	1 M Na^+	2 M Na^+	3 M Na^+	4 M Na^+	0.1 M H^+	0.3 M H^+	0.5 M H^+
SorX[b]	Eu(III)	100	90	70	42			
	Pd(II)	0.4	8	66	200			
	Zr(IV)	67	560	1700	~5300			
	Cs(I)	~200	~1500					
	Mo(VI)	~200	~1500	~6000				
	Sr(II), Rh(III), Ru(III)	≥500	≥2000	≥8000	≥8000			
SX1[c]	Zr(IV)					1.2	4.7	12
	Pd(II)					0.0045	0.02	0.02
	Pb(II)					0.002	0.004	0.006
	Mn(II)					0.83	1.4	1.9
	Ni(II)					0.003	0.004	0.003
	Co(II)					0.015	0.026	0.040
SX2[c]	Zr(IV)					0.018	0.003	0.001
	RuNO(II)					0.23	0.011	0.001
	Cd(II)					0.001	0.0003	<0.0001
	Pb(II)					0.007	0.005	0.002

[a] SorX is sorption extraction on a solid support impregnated with 33.3 wt % DBTP (11−12 wt % styrene−divinylbenzene polymer, incorporated into 55−56 wt % silica, particle size 40−60 μm), SX1 is solvent extraction with 0.01 M DPTP in kerosene/1-octanol (7/3), and SX2 is solvent extraction with 0.02 M 6-(5,6-dipentyl-1,2,4-triazin-3-yl)bipy + 0.5 M 2-bromodecanoic acid in *tert*-butylbenzene. [b] From Wei, Y.-Z.; Hoshi, H.; Kumagai, M.; Asakura, T.; Morita, Y. J. Alloys Compd. 2004, 374, 447. [c] From Drew, M. G. B.; Foreman, M. R. St. J.; Geist, A.; Hudson, M. J.; Marken, F.; Norman, V.; Weigl, M. Polyhedron 2006, 25, 888.

3.3.5. Effect of Counterion on the Selectivity

As a rule, complexes of N-donors are cationic, and an anion is needed for the formation of an electroneutral extractable species. The effect of the counterion on the Am(III)/Eu(III) separation can be rather pronounced. In the extraction by the bidentate extractant 6-methyl-2-(2-pyridyl)-benzimidazole in xylene/1-butanol (7/3),[101] the separation efficiency decreases in the order thiocyanate $\{4\}^{T6}$ > perchlorate $\{5\}^{T6}$ > iodide $\{5\}^{T6}$ > thenoate $\{5\}^{T6}$. DETP in xylene/1-butanol (7/3)[7] $\{27\}^{T6}$ extracts thiocyanates with a higher $\alpha_{Am/Eu}$ value than nitrates. The separation efficiency of TPTZ in *tert*-butylbenzene[5,6] $\{53\}^{T6}$ is similar in the extraction of 2-bromodecanoates and dinonylnaphthalenesulfonates. Finally, the hexadentate extractant *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethanediamine in 1-octanol $\{58\}^{T6}$ extracts bis(2-ethylhexyl)phosphates[94] with an essentially higher separation and extraction efficiency than those for nitrates.[108]

The extraction efficiency is generally very high when alkanoate counterions are used. This is the case with thenoates, but 2-bromoalkanoates are preferred because their acidity is higher than that of other alkanoic acids. This makes it possible to attain feasible distribution ratios even at rather high concentrations of mineral acids. It is seen in Table 6 that 2-bromodecanoate is unquestionably the most used counterion.

3.3.6. Selectivity with Regard to Other Actinides and Fission Products

Although it may exceed the scope of this review, information is of interest about the separation of Ln(III) and An(III) from some of the elements present in radioactive waste. Few data are available, obtained in extraction chromatography and solvent extraction studies. They are gathered Table 7.

Even if data in Table 7 are not rigorously comparable, there are some striking differences between selectivities of the three extractants. Am(III) is extracted selectively with regard to Zr(IV) by both analogous extractants DPTP and DBTP, but not by the similar extractant 6-(5,6-dipentyl-1,2,4-triazin-3-yl)bipy. It is unexpected that Pd(II) is extracted less effectively than Am(III) by DBTP but more effectively than Am(III) by DPTP. This phenomenon is most probably apparent, caused by slow attainment of the distribution equilibrium in the sorption extraction by DBPA. To be noticed is the high affinity of DPTP and 6-(5,6-dipentyl-1,2,4-triazin-3-yl)bipy to bivalent transition metals.

Of other actinides, Th(IV) is not extractable by 0.013 M DPTP in MiBK from 3 M NH_4NO_3 + 0.05 M HNO_3 (D_{Th} < 0.03) and from 3 M NH_4Cl + 0.05 M HCl ($D_{Th} \ll 0.01$).[9] 6,6′-Bis(5,6-dialkyl-1,2,4-triazin-3-yl)bipyridyl (alkyl = ethyl, butyl, pentyl, and hexyl) and 6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)bipyridyl at 0.01 M in cyclohexanone extract Np(V) moderately ($D_{Np} = 1-3$), U(VI) weakly ($D_U = 0.7-1$), and Th(IV) very weakly ($D_{Th} \approx 0.2$)[110]

3.3.7. The Origin and Prediction of the Selectivity

The selectivity of bipy for U(III) over Ce(III) is additionally caused by π back-donation of the 5f orbital of the U^{3+} ion into the π^* orbitals of the heteroaromatic rings.[59] A stronger π back-bonding interaction is said to exist between the U^{3+} ion and terpy, where the higher strength of the U−N bonds in comparison with the Ce−N bonds is indicated by the U−N distance in crystals being shorter than the Ce−N distance.[63,64] A noticeable covalency contribution is attributed to the binding of the Am^{3+} ion to N atoms of 2-amino-4,6-di(2-pyridyl)-1,3,5-triazine. The higher stability of its 1:1 Am(III) complex $\{135\}^{T3}$, as compared with that of Ln(III) complexes[111] $\{117-133\}^{T3}$, is ascribed to a more exothermic reaction enthalpy (see the deviation of the ΔH value of Am(III) from the ΔH vs ΔS dependence of Ln(III) in Figure 5), which is correlated to the greater degree of covalency of the Am−N bond. Based on DFT calculations, the covalency is seen to originate from charge transfer from the ligand σ-orbitals to the 5f and 6d orbitals of Am^{3+}.[111]

More recently, it has been objected[112] that the calculations in ref 111 do not allow one to distinguish between Ln(III) and An(III) in the assessment of the charge transfer to the f and d orbitals. More advanced DFT calculations in ref 112 show that this donation is slight in 1:3 complexes of La(III) and U(III) with 2,6-di(1,2,4-triazin-3-yl)pyridine, and the higher stability of the U(III) complex is due to a strong back-

donation. Based again on DFT calculations, also the higher stability of the 1:3 complex of U(III) with DMTP with regard to the Ce(III) complex is acribed to a strong back-donation.[113] However, considering the high covalency of the Cm−N bonds, the selectivity of the Cm(III) complexing with regard to La(III) can be predominantly ascribed to donation to the 5f and 6d orbitals of Cm^{3+}.[112]

Contrary to that, another quantum chemistry study implies that the covalent contribution to the actinide(III)−nitrogen bond decreases in the order U(III) > Pu(III) > Am(III) ≈ Cm(III), and the participation of 5f orbitals in the bonding is significant only for U(III). The covalent contribution is larger in the DMTP complexes than in terpy complexes.[114]

The partially covalent character of the An(III)−N bond implicitly suggests that complexes of An(III) possess a higher thermodynamic stability than Ln(III) complexes. The separation efficiency of N-donors is ascribed particularly to this stability difference,[78,115] but it is postulated that the difference need not be due to a higher covalence contribution to the actinide(III)−N bond.[78] The accentuation of the higher stability of An(III) complexes is based on the fact that no substantial dissimilarity has been found between the coordination structure of the DPTP complexes [CmB_3^{3+}] and [EuB_3^{3+}],[78] although the Cm(III) complex is more stable.[115]

Another view is expressed in refs 41 and 82 where the ability of BTPs to form complexes of the type MA_3^{3+} is said to be the cause of their high separation efficiency. Let us remember that other, less effective N-donor extractants do not form higher complexes than MA_2^{3+}. It may be worth mentioning that in DMTP complexes the cooperativity, as defined in ref 58, appears to be positive in the complexation of Eu(III) but is negative in the complexation of Am(III). It is revealed, indeed with a limited reliability, by $\log u^{LL} = +0.4 \pm 0.7$ in 50% MeOH calculated from K_1 and K_2 of the Eu(III) complex $\{31\}^{T3}$ and $\log u^{LL} = -1.0 \pm \geq 0.3$ in 75% MeOH calculated from K_1 to K_3 of the Am(III) complex $\{39\}^{T3}$.

It is not clear whether the ability of BTPs to form 1:3 complexes is due to absence of hydrogen bonds in the complex or to electronic properties. Positive overall Mulliken charge on the atoms of the central ring, as compared with a negative charge on the lateral rings, does not appear to be important for effective actinide(III)/lanthanide(III) separation by BTPs.[41]

Even if the importance of the π back-bonding interactions is not questioned, it is suggested that they alone may not exclusively be responsible for the selective bonding of An(III) by N-donors. Also steric factors can play a role. This was concluded from the fact that a shorter U−N bond distance than the La−N, Ce−N, and Nd−N bond distances had been found in four pyrazinyl compounds, namely, tris(2-pyrazylmethyl)amine[92] $\{174,177\}^{T8}$, *N*,*N*,*N*′,*N*′-tetrakis(2-pyrazylmethyl)-1,2-ethanediamine[109] $\{188\}^{T8}$, *N*,*N*,*N*′,*N*′-tetrakis(2-pyrazylmethyl)-1,3-propanediamine[95] $\{190-192,194\}^{T8}$, and *N*,*N*,*N*′,*N*′-tetrakis(2-pyrazylmethyl)-*trans*-1,2-diaminocyclohexane[95] $\{195-198\}^{T8}$, but only the first two of them $\{60,65\}^{T6}$ but not the last two $\{66,67\}^{T6}$ are selective for Am(III) over Eu(III).[95] Notice that a high selectivity is exhibited by N-donors containing in the molecule either one aliphatic N atom or two ones separated by an ethylene bridge. On the other hand, N-donors containing two N atoms either separated by a propylene bridge or attached in vicinal positions to a cyclohexane ring are not selective. The lack of selectivity in the cyclohexane N-donor may be somewhat surprising, because its two N atoms are separated by a $-CH_2-CH_2-$ link similar to an ethylene bridge. The obvious cause is the localization of the N atoms in *trans*-positions, and the circumstance that the $-CH_2-CH_2-$ link is an integral part of an alicyclic ring.

To obtain basic insight into the actinide(III)/lanthanide(III) selectivity of heterocyclic chelating N-donors, complexant properties of heterocyclic rings as their structural constituents were investigated with M = U(III) and Ce(III). The heterocyclic ring, °B, was incorporated into a metallocene complexes of the type [M(°B)($C_5H_4R)_3$] with R being *tert*-butyl and trimethylsilyl. The U−N bond distances in crystal state were shorter than the Ce−N bond distances, and ^{1}H NMR measurement in toluene-d_8 sustained that U(III) formed more stable complexes than Ce(III). With R = trimethylsilyl, the selectivity for U(III) decreased in the °B order dimethylpyrazine > pyrimidine > pyridine > picoline > lutidine > pyridazine ≈ pyrazine ≈ triazine. The same order was found with R = *tert*-butyl except picoline ≈ lutidine. There is a good linear correlation of this order with the $E_{1/2}$ value of the heterocycles, which is taken as an equivalent of the energy of the lowest unoccupied π molecular orbital.[116]

To acquire a possibility of predicting actinide(III)/lanthanide(III) separation factors, quantitative structure−activity relationships (QSAR) were developed that relate the $\alpha_{An/Ln}$ of a series of N-donors to electronic and steric molecular descriptors. Simple relations of the type $\log \alpha_{An/Ln} = p_0 + p_1\varphi_1 + ... + p_i\varphi_i$ were used with p being parameters, φ being the descriptors and $i = 2-4$. To optimize and test the model, data on 47 extractants, as published earlier,[100] were utilized. The optimum molecular descriptors were chosen out of ~1100 values, and the parameters were found with a training set of 36 $\alpha_{An/Ln}$ values. The relations were validated with a test set of 11 $\alpha_{An/Ln}$ values. The optimum equation is $\log \alpha_{An/Ln} = 7.8282 + 1.37269\varphi_1 + 2.31257\varphi_2 - 6.21907\varphi_3$, where φ_1 is the highest eigenvalue no. 5 of Burden matrix weighted by Sanderson electronegativities, φ_2 is the Geary autocorrelation-lag6 weighted by atomic van der Waals volume, and φ_3 is the lowest eigenvalue no. 5 of Burden matrix weighted by atomic polarizability.[117] The ratio of the calculated to experimental $\alpha_{An/Ln}$ values is 0.36 to 2.6 within the training set and 0.45 to 1.7 within the test set.

Using the same data[100] with one extractant excluded, quantitative structure−property relationships (QSPR) modeling was alternatively done to predict $\alpha_{An/Ln}$ values. Also in this case the data were split into a training set (36 compounds) and a test set (10 compounds). A good fit was obtained with a linear regression relation involving six parameters. Two of them were molecular descriptors, namely, polarity parameter and relative negative charge, taken from a pool of 421 parameters. The other four parameters (out of 111) were substructural molecular descriptors. The model was used for the prediction of $\alpha_{An/Ln}$ of a compound not involved in the optimization of the relation, namely, 6-(5-*tert*-butyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl. The calculated separation factor was 1.2−2.9 times higher than the experimental value, depending on the computational method. Within the sum of the training and test sets, the ratio of the calculated to experimental $\alpha_{An/Ln}$ values was in the optimum case 0.6−1.8.[118]

3.3.8. Significance of Bond Distances

It is seen in paragraph 3.3.7 that the character of metal to nitrogen bonds has in many cases been assessed as a source of

Table 8. Metal−nitrogen Bonding Distances in Various Metal Complexes[a]

no.	B	metal complex/coordination number	$M-N_{central}$, Å	$M-N_{lateral}$, Å
1	bipy	$[CeB_2(py)I_3]/8$[59]	2.67 (avgall fourN)	
2		$[UB_2(py)I_3]/8$[59]	2.65 (avgall fourN)	
3	2,6-bis(5-methyl-1,2,4-triazol-3-yl)pyridine	**$[LaB(H_2O)_5(NO_3)^{2+}][NO_3^-]_2\cdot H_2O/10$**[125]	2.774	2.713−2.724
4		**$[NdB(H_2O)(NO_3)_3]\cdot MeCN\cdot 2H_2O/10$**[125]	2.697	2.629
5		**$[SmB(H_2O)(NO_3)_3]\cdot MeCN\cdot 2H_2O/10$**[125]	2.687	2.594
6		**$[TbB(H_2O)(NO_3)_3]\cdot MeCN\cdot 2H_2O/10$**[125]	2.626	2.582
7		**$[HoB(H_2O)(NO_3)_3]\cdot MeCN/9$**[125]	2.518	2.460−2.462
8		**$[YbB(NO_3)_3]\cdot MeCN/9$**[125]	2.497	2.414−2.433
9	terpy	$[LaB_2(NO_3)_2^+][LaB(NO_3)_4^-]/10,11$[60]		
		1st B in **$[LaB_2(NO_3)_2^+]$**	2.681	2.649−2.673
		2nd B in *$[LaB_2(NO_3)_2^+]$*	2.685	2.674−2.736
		B in *$[LaB(NO_3)_4^-]$*	2.709	2.705−2.769
10		**$[LaB(H_2O)_3(NO_3)_2^-][NO_3^-]/10$**[123]	2.688	2.632−2.667
11		*$[LaB(MeOH)_2(NO_3)_3]/11$*[123]	2.700	2.688−2.715
12		**$[LaB(H_2O)_5Cl^{2+}][Cl^-]_2\cdot 3H_2O/9$**[121]	2.688	2.658
13		$[LaB_3^+][I^-]_3\cdot 2MeCN/9$[64]		
		1st B in **$[LaB_3^+]$**	2.683	2.639−2.654
		2nd B in $[LaB_3^+]$	2.689	2.719
14		$[LaB_3^{3+}][ClO_4^-]_3\cdot 2MeCN\cdot 0.67H_2O/9$[b]		
		1st B in $[LaB_3^{3+}]$	2.66	2.67−2.72
		2nd B in *$[LaB_3^{3+}]$*	2.7	2.68−2.79
		3rd B in **$[LaB_3^{3+}]$**	2.73	2.69−2.69
15		**$[CeB(H_2O)_5Cl^{2+}][Cl^-]_2\cdot 3H_2O/9$**[121]	2.658	2.643
16		$[CeB_2I_2^+][I^-]/8$[63]		
		1st B in *$[CeB_2I_2^+]$*	2.636	2.597−2.662
		2nd B in *$[CeB_2I_2^+]$*	2.641	2.614−2.658
17		$[CeB_2I_2^+][I^-]/8$[c]		
		1st B in **$[CeB_2I_2^+]$**	2.636	2.597−2.621
		2nd B in *$[CeB_2I_2^+]$*	2.641	2.614−2.658
18		$[CeB_2(H_2O)I_2^+][I^-]/9$[63]		
		1st B in **$[CeB_2(H_2O)I_2^+]$**	2.691	2.652−2.673
		2nd B in **$[CeB_2(H_2O)I_2^+]$**	2.692	2.665−2.686
19		$[CeB_2(H_2O)I_2^+][I^-]\cdot 2py/9$[c]		
		first B in **$[CeB_2(H_2O)I_2^+]$**	2.685	2.671−2.682
		2nd B in **$[CeB_2(H_2O)I_2^+]$**	2.685	2.655−2.670
20		$[CeB_2(py)(OSO_2CF_3)_2^+][OSO_2CF_3^-]\cdot 0.5py/9$[119]		
		1st B in *$[CeB_2(py)(OSO_2CF_3)_2^+]$*	2.653	2.647−2.656
		2nd B in **$[CeB_2(py)(OSO_2CF_3)_2^+]$**	2.653	2.634−2.640
21		$[CeB_2(H_2O)(OSO_2CF_3)_2^+][OSO_2CF_3^-]\cdot 2py/9$[119]		
		1st B in *$[CeB_2(H_2O)(OSO_2CF_3)_2^+]$*	2.674	2.648−2.679
		2nd B in *$[CeB_2(H_2O)(OSO_2CF_3)_2^+]$*	2.675	2.655−2.676
22		$[CeB_2(OSO_2CF_3)_3]/9$[119]		
		1st B in **$[CeB_2(OSO_2CF_3)_3]$**	2.677	2.632−2.651
		2nd B in *$[CeB_2(OSO_2CF_3)_3]$*	2.653	2.637−2.699
23		$[CeB_2(OSO_2CF_3)_3]\cdot MeCN/9$[119]		
		1st B in **$[CeB_2(OSO_2CF_3)_3]$**	2.702	2.644−2.682
		2nd B in *$[CeB_2(OSO_2CF_3)_3]$*	2.653	2.620−2.663
24		$[CeB_3^{3+}][I^-]_3\cdot 2MeCN/9$[64]		
		1st B in **$[CeB_3^{3+}]$**	2.657	2.613−2.626
		2nd B in $[CeB_3^{3+}]$	2.667	2.695
25		$[CeB_3^{3+}][I^-]_3\cdot 3MeCN/9$[64]		
		1st B in **$[CeB_3^{3+}]$**	2.674	2.646
26		$[CeB_3^{3+}][ClO_4^-]_3\cdot MeCN/$**9**[b]		
		1st B in $[CeB_3^{3+}]$	2.622	2.676−2.679
		2nd B in *$[CeB_3^{3+}]$*	2.631	2.622−2.654
		3rd B in $[CeB_3^{3+}]$	2.635	2.638−2.652
27		$[CeB(cyclopentadienyl)_2^+][I^-]$[65]	2.640	2.565−2.586
28		**$[NdB(H_2O)(NO_3)_3]/10$**[104]	2.703	2.586−2.625
29		$[NdB_2I_2^+][I^-]/8$[c,63]		
		1st B in *$[NdB_2I_2^+]$*	2.594	2.570−2.630
		2nd B in *$[NdB_2I_2^+]$*	2.595	2.577−2.626
30		**$[NdB(H_2O)_5Cl^{2+}][Cl^-]_2\cdot 3H_2O/9$**[121]	2.622	2.613
31		$[NdB_3^+][I^-]_3\cdot 2MeCN/9$[64]		
		1st B in **$[NdB_3^+]$**	2.618	2.587−2.617
		2nd B in $[NdB_3^+]$	2.637	2.676
32		$[NdB_2(NO_3)_2^+][NdB(NO_3)_4^-]$ /10,10[104]		
		1st B in *$[NdB_2(NO_3)_2^+]$*	2.598	2.592−2.631
		2nd B in *$[NdB_2(NO_3)_2^+]$*	2.645	2.638−2.651
		B in *$[NdB(NO_3)_4^-]$*	2.591	2.577−2.600
33		$[NdB_2(py)(OSO_2CF_3)_2^+][OSO_2CF_3^-]\cdot 0.5py/9$[119]		
		1st B in $[NdB_2(py)(OSO_2CF_3)_2^+]$	2.614	2.620−2.623
		2nd B in **$[NdB_2(py)(OSO_2CF_3)_2^+]$**	2.622	2.607−2.615
34		$[NdB_2(OSO_2CF_3)_3]\cdot 0.5MeCN/9$[119]		
		1st B in *$[NdB_2(OSO_2CF_3)_3]$*	2.640	2.619−2.642
		2nd B in **$[NdB_2(OSO_2CF_3)_3]$**	2.631	2.605−2.614

Table 8. Continued

no.	B	metal complex/coordination number	M−$N_{central}$, Å	M−$N_{lateral}$, Å
35	terpy	$[SmB_2(NO_3)_2^+][SmB(NO_3)_4^-]$/10,10[104]		
		1st B in $[SmB_2(NO_3)_2^+]$	2.550	2.583−2.609
		2nd B in *[$SmB_2(NO_3)_2^+$]*	2.621	2.555−2.675
		B in **[$SmB(NO_3)_4^-$]**	2.590	2.556−2.561
36		$[H_2B(NO_3)^+][SmB(NO_3)_4^-]$/11[36]	2.626	2.635−2.650
37		$[SmB(H_2O)_{4.6}Cl^{2+}][Cl^-]_2\cdot 3H_2O$/8−9[121]	2.577	2.571
38		*[$EuB(H_2O)(NO_3)_3$]*/10[124]	2.550	2.538−2.574
39		$[EuB(H_2O)_{4.45}Cl^{2+}][Cl^-]_2\cdot 3H_2O$/8−9[121]	2.542	2.551
40		$[EuB_3^{3+}][ClO_4^-]_3$/9[c]		
		1st B in $[EuB_3^{3+}]$	2.510	2.578
		2nd B in *[EuB_3^{3+}]*	2.579	2.562−2.613
41		$[EuB_3^{3+}][ClO_4^-]_3\cdot$MeCN/9[c]		
		1st B in $[EuB_3^{3+}]$	2.533	2.61−2.611
		2nd B in $[EuB_3^{3+}]$	2.555	2.554−2.598
		3rd B in $[EuB_3^{3+}]$	2.560	2.564−2.59
42		$[GdB(H_2O)_3(NO_3)_2^-][NO_3^-]$/10[123]	2.52	2.53−2.56
43		**[$GdB(H_2O)_3(NO_3)_2^-$]**$[NO_3^-]$[d]	2.546	2.583
44		$[GdB(H_2O)_{4.1}Cl^{2+}][Cl^-]_2\cdot 3H_2O$/8[121]	2.536	2.538
45		*[$TbB(H_2O)(NO_3)_3$]*/10[124]	2.546	2.539−2.564
46		$[TbB_2(NO_3)_2^+][TbB(NO_3)_4^-]$/10,10[104]		
		1st B in $[TbB_2(NO_3)_2^+]$	2.541	2.542−2.567
		2nd B in $[TbB_2(NO_3)_2^+]$	2.586	2.585−2.587
		B in $[TbB(NO_3)_4^-]$	2.513	2.519−2.528
47		$[TbB(H_2O)_2(NO_3)_2^-][NO_3^-]\cdot 2H_2O$/9[123]	2.50	2.50−2.52
48		$[TbB(H_2O)_4Cl^{2+}][Cl^-]_2\cdot 3H_2O$/8[121]	2.509	2.518
49		$[DyB_2(NO_3)_2^+][DyB(NO_3)_4^-]$/10,10[104]		
		1st B in *[$DyB_2(NO_3)_2^+$]*	2.555	2.539−2.587
		2nd B in *[$DyB_2(NO_3)_2^+$]*	2.560	2.528−2.613
		B in *[$DyB(NO_3)_4^-$]*	2.554	2.506−2.527
50		$[DyB(H_2O)_4Cl^{2+}][Cl^-]_2\cdot 3H_2O$/8[121]	2.498	2.511
51		$[HoB_2(NO_3)_2^+][HoB(NO_3)_4^-]$/10,10[104]		
		1st B in *[$HoB_2(NO_3)_2^+$]*	2.545	2.538−2.558
		2nd B in *[$HoB_2(NO_3)_2^+$]*	2.560	2.541−2.605
		B in **[$HoB(NO_3)_4^-$]**	2.544	2.531−2.541
52		**[$HoB(H_2O)(NO_3)_3]\cdot B$**/10[104]	2.545	2.503−2.510
53		$[HoB(H_2O)_4Cl^{2+}][Cl^-]_2\cdot 3H_2O$/8[121]	2.485	2.503
54		**[$ErB(H_2O)(NO_3)_3]\cdot B$**/10[104]	2.505	2.478−2.489
55		*[$ErB(EtOH)(NO_3)_3$]*/9[e]	2.474	2.456−2.485
56		$[ErB(H_2O)_4Cl^{2+}][Cl^-]_2\cdot 3H_2O$/8[121]	2.473	2.496
57		$[TmB(H_2O)(NO_3)_3]\cdot B$/10[104]	2.463	2.475−2.494
58		*[$TmB(H_2O)(NO_3)_3$]*/9[104]	2.482	2.441−2.526
59		$[TmB(H_2O)_4Cl^{2+}][Cl^-]_2\cdot 2H_2O$/8[121]	2.470	2.475−2.532
60		$[YbB(H_2O)_4Cl^{2+}][Cl^-]_2\cdot 3H_2O$/8[121]	2.443	2.451−2.476
61		$[YbB(NO_3)_3]$/9[104]	2.395	2.417−2.419
62		*[$YbB(EtOH)(NO_3)_3$]*/9[61]	2.457	2.446−2.462
63		**[$YbB(H_2O)_2(NO_3)_2][NO_3^-]\cdot 2H_2O$**/9[61]	2.483	2.464−2.468
64		$[LuB(H_2O)_4Cl^{2+}][Cl^-]_2\cdot 3H_2O$/8[121]	2.445	2.463
		[$LuB(H_2O)_4Cl^{2+}$]$[Cl^-]_2\cdot 3H_2O$/8[121] (different structures)	2.443	2.436−2.478
65		$[LuB(NO_3)_3]$/9[61]	2.379	2.395−2.407
66		*[$LuB(EtOH)(NO_3)_3$]*/9[61]	2.455	2.444−2.477
67		**[$LuB(H_2O)_2(NO_3)_2^+$] [NO_3^-]$\cdot 2H_2O$**/9[123]	2.474	2.469−2.472
68		$[LuB(H_2O)(EtOH)(NO_3)_2^+]$ $[NO_3^-]\cdot$EtOH/9[61]	2.465	2.456−2.474
69		$[LuB_3^{3+}][ClO_4^-]_3$/9[c]		
		1st B in $[LuB_3^{3+}]$	2.437	2.502
		2nd B in $[LuB_3^{3+}]$	2.491	2.498−2.553
70		**[$YB(H_2O)_2(NO_3)_2^-$]**$[NO_3^-]\cdot 2H_2O$/9[123]	2.514	2.48−2.49
71		$[YB(H_2O)_4Cl^{2+}][Cl^-]_2\cdot 2H_2O$/8[121]	2.497	2.503−2.551
72		$[YB_3^{3+}][ClO_4^-]_3$/9[c]		
		1st B in $[YB_3^{3+}]$	2.469	2.532
		2nd B in $[YB_3^{3+}]$	2.535	2.524−2.577
73		$[UB_2(py)I_2^+][I^-]$/9[63]		
		1st B in $[UB_2(C_6H_5N)I_2^+]$	2.602	2.625−2.631
		2nd B in $[UB_2(C_6H_5N)I_2^+]$	2.618	2.624−2.657
74		$[UB_3^{3+}][I^-]_3\cdot 2$MeCN/9[64]		
		1st B in $[UB_3^{3+}]$	2.622	2.679
		2nd B in **[UB_3^{3+}]**	2.625	2.592−2.622
75		[UB (cyclopentadienyl)$_2^+$][I^-][65]	2.419	2.428
76		$[UB_2(py)(OSO_2CF_3)_2^+][OSO_2CF_3^-]\cdot$0.5py/9[119]		
		1st B in $[UB_2(py)(OSO_2CF_3)_2^+]$	2.618	2.619−2.635
		2nd B in *[$UB_2(py)(OSO_2CF_3)_2^+$]*	2.624	2.606−2.639
77	terpy	$[UB_2(OSO_2CF_3)_3]\cdot$MeCN/9[119]		
		1st B in **[$UB_2(OSO_2CF_3)_3$]**	2.654	2.617−2.647
		2nd B in **[$UB_2(OSO_2CF_3)_3$]**	2.634	2.606−2.634

Table 8. Continued

no.	B	metal complex/coordination number	M−$N_{central}$, Å	M−$N_{lateral}$, Å
78	2,6-di(2-benzimidazolyl)pyridine	$[CeB_2(NO_3)_2^+][NO_3^-]\cdot 3MeOH/10^f$		
		1st B in **$[CeB_2(NO_3)_2^+]$**	2.687	2.608−2.613
		2nd B in *$[CeB_2(NO_3)_2^+]$*	2.635	2.629−2.699
79		$[EuB_2(NO_3)_2^+][NO_3^-]\cdot 2MeOH/10^f$		
		1st B in **$[EuB_2(NO_3)_2^+]$**	2.609	2.51−2.551
		2nd B in **$[EuB_2(NO_3)_2^+]$**	2.633	2.567−2.592
80		$[TbB_2(NO_3)_2^+][NO_3^-]\cdot 2MeOH/10^f$		
		1st B in **$[TbB_2(NO_3)_2^+]$**	2.583	2.500−2.518
		2nd B in **$[TbB_2(NO_3)_2^+]$**	2.590	2.535−2.549
81	2,6-bis(1-methylbenzimidazol-2-yl)pyridine	**$[EuB(MeOH)(NO_3)_3]$**/10^g	2.611	2.477−2.537
82	2,6-bis[1-(1-*S*-neopentyl)benzimidazol-	**$[EuB(MeCN)(NO_3)_3]$**/10^h	2.627	2.470−2.470
83	2-yl]pyridine	$[EuB_3^{3+}][ClO_4^-]_3\cdot 4MeCN/9^{26}$		
		1st B in $[EuB_3^{3+}]$	2.547	2.573−2.583
		2nd B in $[EuB_3^{3+}]$	2.567	2.591−2.621
		3rd B in *$[EuB_3^{3+}]$*	2.598	2.570−2.609
84	2,6-bis(1-octylbenzimidazol-2-yl)pyridine	**$[EuB(NO_3)_3]$**/9^g	2.598	2.473−2.491
85	2,6-bis(1-ethyl-5-methylbenzimidazol-	$[EuB_3^{3+}][ClO_4^-]_3\cdot 4MeCN/9^{76}$		
	2-yl)pyridine	1st B in $[EuB_3^{3+}]$	2.53	2.61−2.66
		2nd B in $[EuB_3^{3+}]$	2.56	2.59−2.61
		3rd B in **$[EuB_3^{3+}]$**	2.60	2.56−2.59[3]
86	4-(4-nitrophenyl)-2,6-bis[1-	**$[EuB(MeCN)(NO_3)_3]\cdot 2.5MeCN$**/$10^i$	2.629	2.526−2.554
	(3,5-dimethoxybenzyl)benzimidazol-2-			
	yl]pyridine			
87	2,6-di(2-benzoxazolyl)pyridine	$[LaB(H_2O)_2(NO_3)_3]/11^{103}$	2.744	2.770−2.781
88		**$[PrB(MeCN)(NO_3)_3]$**/10^{103}	2.715	2.664−2.669
89		**$[NdB(MeCN)(NO_3)_3]$**/10^{103}	2.720	2.654−2.667
90		**$[ErB(MeCN)(NO_3)_3]$**/10^{103}	2.617	2.545−2.564
91		*$[EuB(H_2O)(NO_3)_3]$*/10^{103}	2.657	2.625−2.699
92		*$[GdB(H_2O)(NO_3)_3]$*/10^{103}	2.640	2.588−2.679
93	2,6-bis(1,2,4-triazin-3-yl)-pyridine	$[NdB_2(NO_3)_3]/12^j$	2.70−2.77	
94		$[PrB_2(NO_3)_3]/12^j$	2.731−2.754	
95	DMTP	$[LaB_3^{3+}][OSO_2CF_3^-]_3\cdot MeCN/9^{64}$		
		1st B in **$[LaB_3^{3+}]$**	2.646	2.624−2.629
		2nd B in **$[LaB_3^{3+}]$**	2.675	2.608−2.617
		3rd B in **$[LaB_3^{3+}]$**	2.686	2.651−2.655
96		$[CeB_3^{3+}][I^-]_3\cdot 9py/9^{99}$		
		1st B in *$[CeB_3^{3+}]$*	2.624	2.598−2.625
		2nd B in **$[CeB_3^{3+}]$**	2.641	2.613
97		$[CeB_3^{3+}][OSO_2CF_3^-]_3\cdot MeCN/9^{64}$		
		1st B in $[CeB_3^{3+}]$	2.620	2.605−2.619
		2nd B in **$[CeB_3^{3+}]$**	2.633	2.573−2.611
		3rd B in **$[CeB_3^{3+}]$**	2.658	2.620−2.625
98		$[CeB_3^{3+}][OSO_2CF_3^-]_2[I^-]\cdot 2py/9^{64}$		
		1st B in $[CeB_3^{3+}]$	2.626	2.628−2.629
		2nd B in **$[CeB_3^{3+}]$**	2.655	2.600−2.609
		3rd B in **$[CeB_3^{3+}]$**	2.668	2.595−2.609
99		**$[Nd_2B_2(NO_3)_6]$**/10^k	2.644	2.604−2.618
100	DETP	**$[NdB(C_2H_5OH)(NO_3)_3]$**/10^k	2.641	2.612
101	DPTP	$[CeB_3^{3+}][I^-]_3\cdot 3py/9^{64}$		
		1st B in *$[CeB_3^{3+}]$*	2.63	2.57−2.64
		2nd B in *$[CeB_3^{3+}]$*	2.65	2.61−2.66
		3rd B in **$[CeB_3^{3+}]$**	2.65	2.54−2.59
102		$[SmB_3^{3+}][Sm(NO_3)_5^{2-}]_{1.5}/9$,[l] range of distances in $[SmB_3^{3+}]$	2.556−2.587	2.567−2.595
103		$[TmB_3^{3+}][Tm(NO_3)_4(H_2O)_2^-][NO_3^-]_2/9$,[l] range of distances in $[TmB_3^{3+}]$	2.483−2.490	2.486−2.522
104		$[YbB_3^{3+}][NO_3^-]_3/9$ and $[YbB_3^{3+}][Yb(NO_3)_5^{2-}][Yb(C_2H_5OH)(NO_3)_4^-]\cdot H_2O\cdot C_2H_5OH/9$,[l] range of distances in $[YbB_3^{3+}]$	2.450−2.481	2.458−2.499
105		$[UB_3^{3+}][I^-]_3\cdot 4py/9^{64}$		
		1st B in $[UB_3^{3+}]$	2.53	2.53−2.56
		2nd B in **$[UB_3^{3+}]$**	2.56[2]	2.52−2.53
		3rd B in *$[UB_3^{3+}]$*	2.56	2.54−2.57
106	DiBTP	$[NdB_2(NO_3)_2^+][NO_3^-]/10^k$	2.66−2.68	2.59−2.63
107	2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-	$[YB_3^{3+}][Y(NO_3)_5^{2-}][NO_3^-]/9^{42}$		
	tetrahydrobenzo-1,2,4-	1st B in *$[YB_3^{3+}]$*	2.470	2.451−2.511
	triazin-3-yl)bipyridyl	2nd B in $[YB_3^{3+}]$	2.461	2.476−2.522
		3rd B in $[YB_3^{3+}]$	2.426	2.493−2.507
108	6,6′-bis(5,6-diethyl-1,2,4-	**$[LaB(NO_3)_3]$**/10^{44}	2.741	2.704
109	triazin-3-yl)-2,2′-bipyridyl	**$[CeB(NO_3)_3]$**/10^{44}	2.699	2.674
110		**$[PrB(NO_3)_3]$**/10^{44}	2.660	2.650
111		$[NdB(NO_3)_3]/10^{44}$	2.635	2.639
112		$[SmB(NO_3)_3]/10^{44}$	2.595	2.617
113		$[EuB(NO_3)_3]/10^{44}$	2.604	2.602
114		$[DyB(NO_3)_3]/10^{44}$	2.477−2.521	2.538−2.521
115		$[HoB(NO_3)_3]/10^{44}$	2.487−2.505	2.514−2.509

Table 8. Continued

no.	B	metal complex/coordination number	$M-N_{central}$, Å	$M-N_{lateral}$, Å
116	6,6′-bis(5,6-diethyl-1,2,4-	$[ErB(NO_3)_3]/10$[44]	2.383−2.508	2.530−2.521
117	triazin-3-yl)-2,2′-bipyridyl	$[YbB(NO_3)_3]/10$[44]	2.438−2.450	2.439−2.461
118		$[LuB(H_2O)(NO_3)_2^+][NO_3^-]/9$[44]	2.433−2.448	2.447−2.457
119		$[YB(NO_3)_3]/10$[44]	2.499−2.516	2.515−2.525
120	4-amino-2,6-di(2-pyridyl)-1,3,5-triazine	$[LaB(H_2O)(NO_3)_3]\cdot MeCN/10$[82]	2.576	2.625−2.641
121		$[PrB(H_2O)(NO_3)_3]\cdot MeCN/10$[82]	2.541	2.597−2.600
122		$[NdB(H_2O)(NO_3)_3]\cdot 2MeCN/10$[82]	2.552	2.618−2.645
123		$[NdB(H_2O)_3(NO_3)_2^+][NO_3^-]\cdot H_2O/10$[82]	2.575	2.605−2.630
124		$[SmB(H_2O)(NO_3)_3]\cdot MeCN/10$[82]	2.523	2.578−2.602
125		$[SmB(H_2O)_3(NO_3)_2^+][NO_3^-]\cdot H_2O/10$[82]	2.542	2.561−2.590
126		$[EuB(H_2O)_2(NO_3)_2^+][NO_3^-]\cdot 2H_2O/9$[82]	2.532	2.580−2.590
127		$[GdB(H_2O)_2(NO_3)_2^+][NO_3^-]\cdot H_2O\cdot MeCN/9$[82]	2.460	2.541−2.549
128		$[TbB(H_2O)_2(NO_3)_2^+][NO_3^-]\cdot 2H_2O/9$[82]	2.515	2.569−2.575
129		$[HoB(H_2O)_2(NO_3)_2^+][NO_3^-]\cdot 3H_2O/9$[82]	2.463	2.499−2.561
130		$[ErB(H_2O)_2(NO_3)_2^+][NO_3^-]\cdot H_2O\cdot MeCN/9$[82]	2.460	2.519−2.553
131		$[TmB(H_2O)_2(NO_3)_2^+][NO_3^-]/9$[82]	2.434	2.512−2.539
132		$[YbB(H_2O)(NO_3)_3]\cdot 2MeCN/10$[82]	2.425	2.506−2.517
133		$[YbB(H_2O)_2(NO_3)_2^+][NO_3^-]\cdot 2H_2O/9$[82]	2.423	2.484−2.522
134		$[LuB(H_2O)_2(NO_3)_2^+][NO_3^-]\cdot 2H_2O/9$[82]	2.435	2.493−2.530
135		$[YB(H_2O)(NO_3)_3]\cdot 2MeCN/9$[82]	2.452	2.539−2.552
136	TPTZ	*[LaB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.691	2.667−2.703
137		$[CeB_2(H_2O)I_2^+][I^-]\cdot 3py/9$[c]		
		1st B in $[NdB(py)I_2^+]$	2.636	2.658−2.720
		2nd B in $[NdB(py)I_2^+]$	2.645	2.692−2.715
138		$[CeB(H_2O)(NO_3)_3]/10$[127]	2.66	2.70
139		*[CeB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.678	2.660−2.696
140		*[PrB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.644	2.630−2.668
141		*[PrB(CH₃COO)₃]₂*·2CH₃OH/10[86]	2.687	2.674−2.717
142		$[NdB_2(py)I_2^+][I^-]/9$[c]		
		1st B in $[NdB(py)I_2^+]$	2.600	2.643−2.684
		2nd B in $[NdB(py)I_2^+]$	2.618	2.690−2.693
143		*[NdB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.629	2.614−2.658
144		*[SmB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.603	2.593−2.629
145		*[EuB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.579	2.576−2.619
146		$[EuB(CH_3OH)_2Cl_3]\cdot CH_3OH/8$[86]	2.555	2.617−2.646
147		$[GdB(H_2O)(NO_3)_3]/10$[127]	2.54	2.59−2.63
148		*[GdB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.569	2.567−2.607
149		*[TbB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.555	2.545−2.592
150		*[DyB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.547	2.534−2.582
151		*[HoB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.536	2.524−2.573
152		*[ErB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.528	2.513−2.562
153		*[TmB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.508	2.508−2.519
154		*[YbB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.510	2.490−2.541
155		$[LuB(H_2O)(NO_3)_3]/10$[127]	2.43	2.48−2.50
156		*[YB(H₂O)(NO₃)₃]*·2C₂H₅OH/10[126]	2.539	2.529−2.578
157	tris(2-pyridylmethyl)amine	**[LaB(py)I₃]**/8[88]	2.712	2.670−2.676
158		$[LaB_2^{3+}][I^-]_3/8$[87]		
		1st B in *[LaB₂³⁺]*	2.651	2.629−2.700
		2nd B in *[LaB₂³⁺]*	2.654	2.634−2.680
159		$[CeBI_3]/7$[87]	2.615	2.619−2.671
160		$[CeB_2^{3+}][I^-]_3/8$[87]		
		1st B in $[CeB_2^{3+}]$	2.620	2.608−2.665
		2nd B in $[CeB_2^{3+}]$	2.621	2.610−2.666
161		$[CeB(\mu\text{-}OH)(MeCN)(H_2O)^{2+}]_2[I^-]_4/$**8**[87]	2.690	2.630−2.676
162		$[NdB_2^{3+}][I^-]_3/$**8**[87]		
		1st B in *[NdB₂³⁺]*	2.586	2.581−2.617
		2nd B in *[NdB₂³⁺]*	2.590	2.574−2.615
163		*[NdB(MeOH)Cl₃]*·CH₃OH/8[89]	2.668	2.601−2.702
164		**[EuBCl₃]**/7[89]	2.612	2.556−2.588
165		*[EuB(OSO₂CF₃)₂(H₂O)₂]*/9[87]	2.628	2.575−2.682
166		$[EuB_2^{3+}][OSO_2CF_3^-]_3/8$[87]		
		1st B in *[EuB₂³⁺]*	2.554	2.522−2.564
		2nd B in **[EuB₂³⁺]**	2.560	2.528−2.548
167		*[EuB(μ-OH)(OSO₂CF₃)₂]₂*/8[87]	2.639	2.578−2.730
168		**[TbBCl₃]**/7[89]	2.568	2.513−2.545
169		**[LuBCl₃]**/7[89]	2.555	2.491−2.519
170		$[LuB_2^{3+}][I^-]_3/8$[87]		
		1st B in *[LuB₂³⁺]*	2.487	2.465−2.511
		2nd B in *[LuB₂³⁺]*	2.490	2.469−2.514
171		*[UB(py)I₃]*/8[88]	2.663	2.629−2.67
172	tris[(2,2′-bipyrid-6-yl)methyl]amine	*[LaB(H₂O)(η²-ClO₄)²⁺]*$[ClO_4^-]_2\cdot 2CHCl_3\cdot MeOH/9$[93]	2.723	2.688−2.797
173		**[UBI₂⁻]**$[I^-]\cdot py/10$[93]	2.697	2.595−2.657
174	tris(2-pyrazylmethyl)amine	*[LaB(MeCN)I₃]*·MeCN/8[92]	2.715	2.691−2.723
175		*[LaB(THF)I₃]*·THF/8[92]	2.732	2.705−2.798

Table 8. Continued

no.	B	metal complex/coordination number	M−$N_{central}$, Å	M−$N_{lateral}$, Å
176	tris(2-pyrazylmethyl)amine	*[NdB(H$_2$O)$_3$(MeCN)$_3$]*[ClO_4^-]$_3$·H$_2$O/10[89]	2.734	2.719−2.770
177		*[UB(MeCN)I$_3$]*·MeCN/8[92]	2.721	2.672−2.726
178		*[UB(THF)I$_3$]*·THF/8[92]	2.685	2.657−2.756
179	bis(2-pyridylmethyl)(2-	**[EuB(NO$_3$)$_3$]**/10*[m]*	2.718	2.618−2.682
180	benzimidazolylmethyl)amine	**[GdB(NO$_3$)$_3$]**/10*[m]*	2.717	2.622−2.717
181		**[TbB(NO$_3$)$_3$]**/10*[m]*	2.662	2.581−2.648
182	(2-pyridylmethyl)bis(2-	**[PrB(antipyrine)$_3^{3+}$]**[ClO_4^-]$_3$/7*[m]*	2.770	2.520−2.630
183	benzimidazolylmethyl)amine	**[EuB(Ap)(H$_2$O)$_2$Cl^{2+}]**[Cl^-]$_2$·2H$_2$O/8*[m]*	2.728	2.423−2.548
184		**[YB(Ap)$_3^{3+}$]**[ClO_4^-]$_3$/**7***[m]*	2.678	2.440−2.561
185	tris(2-benzimidazolylmethyl)amine	**[CeB(NO$_3$)$_3$]**·H$_2$O/10[91]	2.825	2.603−2.660
186		**[EuB$_2^{3+}$]**[ClO_4^-]$_3$·2MeCN·3Et$_2$O/8[90]	2.713	2.496−2.504
		[EuB$_2^{3+}$][ClO_4^-]$_3$[90]	2.725	2.479−2.507
187		**[ErB(NO$_3$)$_3$]**·H$_2$O/10[91]	2.673	2.525−2.525
188	*N*,*N*,*N*′,*N*′-tetrakis(2-pyrazylmethyl)-	[LaB(MeCN)$_2$I^{2+}][I^-]$_2$·2MeCN/**9**[109]		
	1,2-ethanediamine ($R_2NC_2H_4NR_2$)	1st NR_2 in B in *[LaB(MeCN)$_2$I^{2+}]*	2.698	2.703−2.704
		2nd NR_2 in B in *[LaB(MeCN)$_2$I^{2+}]*	2.734	2.661−2.748
189	*N*,*N*,*N*′,*N*′-tetrakis(2-pyrazylmethyl)-1,3-	[$LaBI_2^+$][I^-]/8[95,109]		
	propanediamine	1st NR_2 in B in *[$LaBI_2^+$]*	2.787	2.680−2.794
	($R_2NC_3H_6NR_2$)	2nd NR_2 in B in **[$LaBI_2^+$]**	2.753	2.731−2.759
190		[$LaBI_2^+$][I^-]·1.17MeCN/8[95,109]		
		1st NR_2 in B in **[$LaBI_2^+$]**	2.704	2.667−2.703
		2nd NR_2 in Bin **[$LaBI_2^+$]**	2.732	2.636−2.671
191		[$CeBI_2^+$][I^-]·1.17MeCN/8[95]		
		1st NR_2 in B in *[$CeBI_2^+$]*	2.678	2.641−2.680
		2nd NR_2 in B in *[$CeBI_2^+$]*	2.705	2.615−2.643
192		[$NdBI_2^+$][I^-]·1.17MeCN/8[95]		
		1st NR_2 in B in **[$NdBI_2^+$]**	2.654	2.608−2.654
		2nd NR_2 in B in **[$NdBI_2^+$]**	2.671	2.578−2.620
193		[LuB(MeCN)$_2^{3+}$][I^-]$_3$·MeCN/8[95]		
		1st NR_2 in B in [LuB(MeCN)$_2^{3+}$]	2.439	2.478−2.483
		2nd NR_2 in B in *[LuB(MeCN)$_2^{3+}$]*	2.480	2.458−2.463
194		[UBI_2^+][I^-]·1.17MeCN/8[95]		
		1st NR_2 in B in **[UBI_2^+]**	2.670	2.623−2.665
		2nd NR_2 in B in **[UBI_2^+]**	2.698	2.593−2.630
195	*N*,*N*,*N*′,*N*′-tetrakis (2-pyrazylmethyl)-1,6-	[$LaBI_2^+$][I^-]·0.5MeCN/8[95]		
	cyclohexanediamine	1st NR_2 in B in *[$LaBI_2^+$]*	2.684	2.646−2.734
	($R_2NC_6H_{12}NR_2$)	2nd NR_2 in B in **[$LaBI_2^+$]**	2.708	2.607−2.704
196		[$CeBI_2^+$][I^-]·0.5MeCN/8[95]		
		1st NR_2 in B in *[$CeBI_2^+$]*	2.653	2.618−2.707
		2nd NR_2 in B in **[$CeBI_2^+$]**	2.681	2.577−2.662
197		[$NdBI_2^+$][I^-]·0.5MeCN/8[95]		
		1st NR_2 in B in *[$NdBI_2^+$]*	2.632	2.601−2.689
		2nd NR_2 in B in *[$NdBI_2^+$]*	2.649	2.549−2.650
198		[UBI_2^+][I^-]·0.5MeCN/8[95]		
		1st NR_2 in B in *[UBI_2^+]*	2.627	2.593−2.685
		2nd NR_2 in B in **[UBI_2^+]**	2.677	2.537−2.659

[a] Relations between bonding distances of the *n*th B are M−$N_{central}$ > M−$N_{lateral(1,2)}$ in boldface species, M−$N_{lateral(1)}$ < M−$N_{central}$ < M−$N_{lateral(2)}$ in italic species, and M−$N_{central}$ < M−$N_{lateral}$ in unmarked species. [b] From Semenova, L. I.; Sobolev, A. N.; Skelton, B. W.; White, A. H. Aust. J. Chem. 1999, 52, 519. [c] From Riviere, C. Ph. D.Thesis, Université de Paris XI, Orsay, France, 2000. [d] From Leverd, P. C.; Charbonnel, M.-C.; Dognon, J.-P.; Lance, M.; Nierlich, M. Acta Crystallogr. 1999, C55, 368. [e] From Cotton, S. A.; Raithby, P. R. Inorg. Chem. Commun. 1999, 2, 86. [f] From Wang, S.; Zhu, Y.; Cui, Y.; Wang; L., Luo, Q. J. Chem. Soc., Dalton Trans. 1994, 2523. [g] From Piguet, C.; Williams, A. F.; Bernardinelli, G.; Moret, E.; Bünzli, J.-C. G. Helv. Chim. Acta 1992, 75, 1697. [h] From Muller, G.; Maupin, C. L., Riehl, J. P.; Birkedal, H.; Piguet, C.; Bünzli, J.-C. G. Eur. J. Inorg. Chem. 2003, 4065. [i] From Petoud, S.; Bünzli, J.-C. G.; Schenk, K. J.; Piguet, C. Inorg. Chem. 1997, 36, 1345. [j] From Boucher, C.; Drew, M. G. B.; Giddings, P.; Harwood, L. M.; Hudson, M. J.; Iveson, P. B.; Madic, C. Inorg. Chem. Commun. 2002, 5, 596. [k] From Drew, M. G. B.; Guillaneux, D.; Hudson, M. J.; Iveson, P. B.; Madic, C. Inorg. Chem. Commun. 2001, 4, 462. [l] From Drew; M. G. B., Guillaneux, D.; Hudson, M. J.; Iveson, P. B.; Russell, M. L.; Madic, C. Inorg. Chem. Commun. 2001, 4, 12. [m] From Yang, X.-P.; Kang, B.-S.; Wong, W.-K.; Su, C.-Y.; Liu, H.-Q. Inorg. Chem. 2003, 42, 169.

information about the properties of metal complexes. Relations between bond distances of different metal ions to a particular N atom of a ligand have been considered as well as those between a particular metal ion and different N atoms of a ligand. Bond distances in various complexes are gathered in Table 8. To characterize the complexes, those ligands that are located in the inner coordination sphere of the metal ion are written within brackets together with the complexed metal. Comparison of the distances in complexes of various metals with a ligand is difficult, because it is not always possible to prepare a series of solids embodying different Ln(III) and strictly the same ligands. For example, even under identical starting conditions, complexes of different Ln^{3+} ions contain various numbers of solvent molecules (MeCN, EtOH, THF, H_2O) inserted into the inner or outer coordination sphere. Data in Table 8 show that the presence of such molecules in the complex entity can influence the bond distances quite markedly.

3.3.9. Comparative An(III)−N and Ln(III)−N Bond Distances

Discussion of relations between M−N bonding distances is mostly based on U−N and Ce−N or La−N distances found by X-ray diffraction in solid complexes. The relevance of comparing the U−N and Ce−N bonding distances is justified by the similar ionic radii of the Ce^{3+} and U^{3+} ions. The U−N bonding distance is generally shorter than expected in a purely ionic bonding mode. The distance in comparable

complexes is shorter than that of the Ce−N bond, which is considered to be of predominantly ionic character.

The differences between bonding distances, Δl_c = (Ln−$N_{central}$) − (U−$N_{central}$) and Δl_l = (Ln−$N_{lateral}$) − (U−$N_{lateral}$), are small in the bipy complexes [$CeB_2(py)I_3$] {*1*}[T8] and [$UB_2(py)I_3$] {*2*}[T8], where the average of the four Ce−N and U−N bonding distances gives $\Delta l_c \approx \Delta l_l = 0.02$ Å.[59]

Larger differences are found in solid planar terpy complexes. In [CeB_3^{3+}][I^-]$_3$·2MeCN {*24*}[T8] and [UB_3^{3+}][I^-]$_3$·2MeCN {*74*}[T8], the bonding distances are[64] $\Delta l_c = 0.032$ Å and $\Delta l_l = 0.004$ and 0.021 Å for the first ligand and $\Delta l_c = 0.045$ Å and $\Delta l_l = 0.016$ Å for the second ligand. In [$CeB_2(py)(OSO_2CF_3)_2^+$][$OSO_2CF_3^-$]·0.5py {*20*}[T8] and [$UB_2(py)(OSO_2CF_3)_2^+$][$OSO_2CF_3^-$]·0.5py {*76*}[T8] the distances are[119] $\Delta l_c = 0.035$ Å and $\Delta l_l = 0.028$ and 0.021 Å for the first ligand and $\Delta l_c = 0.029$ Å and $\Delta l_l = 0.028$ and 0.011 Å for the second ligand. In [$CeB_2(OSO_2CF_3)_3$]·MeCN {*23*}[T8] and [$UB_2(OSO_2CF_3)_3$]·MeCN {*77*}[T8] the distances are $\Delta l_c = 0.048$ Å and $\Delta l_l = 0.027$ and 0.040 Å for the first ligand and $\Delta l_c = 0.019$ Å and $\Delta l_l = 0.014$ and 0.029 Å for the second ligand.

Still larger differences between the bonding lengths are found in the planar DPTP complexes [CeB_3^{3+}][I^-]$_3$·3py[64] {*101*}[T8] and [UB_3^{3+}][I^-]$_3$·4py[99] {*105*}[T8], in coherence with the higher selectivity of ditriazinyl pyridines for Ln(III) over An(III), namely, $\Delta l_c = 0.09$ Å and $\Delta l_l = 0.07$ and 0.09 Å for the first ligand, $\Delta l_c = 0.10$ Å and $\Delta l_l = 0.04$ and 0.08 Å for the second ligand, and $\Delta l_c = 0.09$ Å and $\Delta l_l = 0.02$ and 0.13 Å for the third ligand.

The differences are especially large in terpy/cyclopentadienyl complexes in [$CeB(Cp)_2^+$][I^-] {*27*}[T8] and [$UB(Cp)_2^+$][I^-] {*75*}[T8], where $\Delta l_c = 0.121$ Å and $\Delta l_l = 0.137$ Å. Intramolecular electron transfer may in this case contribute to the shortening of the U−N distances, because U is possibly tetravalent and terpy is possibly in a radical form in a fraction of the U complex.[65]

Intermediate differences are found in nonplanar complexes of tris(2-pyridylmethyl)amine,[88] [$LaB(py)I_3$] {*157*}[T8] and [$UB(py)I_3$] {*171*}[T8], namely, (the amine nitrogen is taken as the central one) $\Delta l_c = 0.049$ Å and $\Delta l_l = 0.041$ and 0.01 Å.

Relativistic DFT calculations emphasize the necessity of comparing M−N bond distances in complexes of the same composition. The calculations predict the M−N distances to be dependent on the coordination surrounding the central M^{3+} ion. With M being La and U and B being terpy, the calculated values are $\Delta l_c = 0.115$ Å and $\Delta l_l = 0.091$ Å in the complexes [$MB(H_2O)_6^{3+}$], $\Delta l_c = 0.166$ Å and $\Delta l_l = 0.144$ Å in [$MB(H_2O)_5Cl^{2+}$], $\Delta l_c = 0.213$ Å and $\Delta l_l = 0.177$ Å in [$MBCl_3$], and $\Delta l_c = 0.287$ Å and $\Delta l_l = 0.186$ Å in [$MB(H_2O)(NO_3)_3$]. Increase of the Δl_c and Δl_l values in the above series of complexes has also been predicted for M = La and Am. Contrary to that, with M = La and Cm, the Δl_c and Δl_l values attain a maximum in the complexes [$MB(H_2O)_5Cl^{2+}$].[120]

The calculations also illustrate the effect of substituents R at the 5,6-positions of the triazinyl rings in the molecule of 2,6-di(1,2,4-triazin-2-yl)pyridine. Taking La and U as M in the complex [$MB(H_2O)_6^{3+}$], the bond distances are $\Delta l_c = 0.149$ Å and $\Delta l_l = 0.123$ Å with R = H, $\Delta l_c = 0.147$ Å and $\Delta l_l = 0.131$ Å with R = CH_3, $\Delta l_c = 0.131$ Å and $\Delta l_l = 0.144$ Å with R = OCH_3, and $\Delta l_c = 0.101$ Å and $\Delta l_l = 0.250$ Å with R = CN.[120]

Relation between bond lengths within molecules or ions of Ce(III) and U(III) terpy complexes is seen as evidence for π back-bonding interactions in the latter but not the former. In the complex cation [$UB_2(py)I_2^+$] {*73*}[T8] the U−$N_{central}$ bonding distance is shorter than U−$N_{lateral}$. Contrary to that, longer Ce−$N_{central}$ distance than the Ce−$N_{lateral}$ distance is observed in the complexes [$CeB_2(H_2O)I_2^+$] {*18,19*}[T8]. Let us notice than not both but only one of the M−$N_{lateral}$ bonding distances may be longer than the M−$N_{central}$ one. So the relation M−$N_{lateral\text{-}1}$ > M−$N_{central}$ > M−$N_{lateral\text{-}2}$ is found in the similar complexes [$MB_2I_2^+$] with M = Ce(III) {*17,18*}[T8] and Nd(III)[63] {*29*}[T8].

Variable location of the π back-bonding is indicated by the bond length relations in octacoordinated complexes of tris(2-pyrazylmethyl)amine with La(III) and U(III), namely, [$MB(MeCN)I_3$]·MeCN (La {*174*}[T8], U {*177*}[T8]) and [$MB(THF)I_3$]·THF (La {*175*}[T8], U {*178*}[T8]). In the acetonitrile adduct, a π back-bonding interaction is designated only between the U^{3+} ion and the acetonitrile N atom. Here the U−$N_{pyrazyl}$ distances are shorter than the La−$N_{pyrazyl}$ distance by as little as 0.019 Å, while the U−N_{MeCN} distance is shorter than the La−N_{MeCN} one by 0.05 Å. Moreover, the C≡N bond is extended with respect to its typical length in complexes. On the other hand, in the tetrahydrofuran adduct, the average U−$N_{pyrazyl}$ distance is shorter by 0.05 Å than the average La−$N_{pyrazyl}$ distance. Since isostructural compounds of ions with similar ionic radii are compared, the results indicate a stronger interaction of the U^{3+} ion with the N atom of acetonitrile in the former case and with those of the N-donor in the latter case. In both cases, there is a covalent contribution to the bond between the U^{3+} ion and the respective N atom. Detailed orbital analysis revealed back-donation electron transfer from 5f orbitals of the U^{3+} ion but not from 4f orbitals of the La^{3+} ion.[92]

Shorter metal−N bond distances in An(III) complexes in comparison with Ln(III) complexes and, thus, a stronger covalent contribution to the An(III)−N bond were also predicted by DFT calculations.[114] Elsewhere the calculations predict very small differences between the Cm−N and Eu−N bonds (≤0.011 Å). In accord with the prediction, the average Cm−N distance (2.57 Å) in the DPTP complexes [MB_3^{3+}] was found by EXAFS to be very similar to the Eu−N distance (2.56 Å), indeed not in solid state but in a solution in TPH/1-octanol (7/3 v/v).[78] Further EXAFS studies of DPTP complexes in the same solvent yielded the distances 2.57 Å for U−N, 2.562 Å for Am−N, 2.554 Å for Gd−N, and 2.52 Å for Lu−N. To take variations of ionic radii into consideration, the difference between the M−N bond distance and the ionic radius of M^{3+} was taken as a measure of the bond strength, that is, the degree of covalence. The difference increases, and thus, the covalence contribution is supposed to decrease in the order U (1.56 Å) < Am (1.60 Å) < Gd (1.61 Å) < Lu (1.67 Å).[115]

3.3.10. Comparative M−N Bond Distances within the Ln(III) and An(III) Series

It is desirable to pay attention to variations of the bonding distances and their ratios also in a series of solid Ln(III) and An(III) complexes, even if they may have no direct impact on An(III)/Ln(III) separation. Some insight can be useful as a contribution to the knowledge of basic chemistry of the

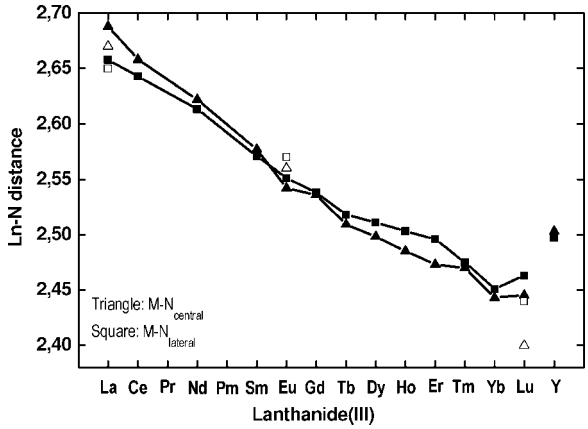


Figure 8. Bond distances between Ln(III) ions and nitrogen atoms in crystals of terpy chloride complexes. Solid points are experimental values for $[TmB(H_2O)_4Cl^{2+}][Cl^-]_2 \cdot 2H_2O$ and $[MB(H_2O)_xCl^{2+}][Cl^-]_2 \cdot 3H_2O$ with $x = 4-5$[122] for other M {*12,15,30,37,39,44,48, 50, 53,56,59,60,64,71*}[T8]. Open points are calculated values.[121]

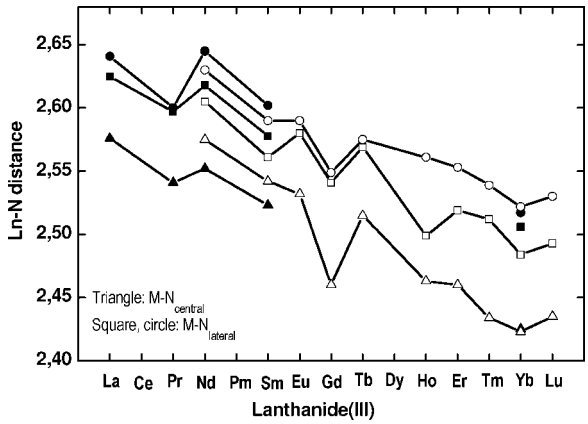


Figure 9. Bond distances between lanthanide(III) ions and nitrogen atoms in crystal complexes of 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine.[79] Solid points are $[MB(H_2O)(NO_3)_3]$ {*120−122,124,132*}[T8]; open points are $[MB(H_2O)_3(NO_3)_2^+][NO_3^-]$ with M = Nd {*123*}[T8] and Sm {*125*}[T8] and $[MB(H_2O)_2(NO_3)_2^+][NO_3^-]$ for other M {*126−131,133,134*}[T8].

two element groups. Cases of both an invariable ligand and an invariable Ln^{3+} ion can be treated.

Generally, in the Ln(III) series, the bonding distances decrease with decreasing ionic radius of the central ion (see Figures 8−10). The phenomenon was also predicted by relativistic DFT calculations. It was done for terpy and DMTP complexes $[MB(H_2O)_6]^{3+}$ and $[MB(H_2O)_5Cl]^{2+}$, in which M is La, Ce, and Nd. Contrary to the Ln(III) group, in the series of the same complexes with M being U, Pu, Am, and Cm, the An−N bonding distance was predicted to increase with decreasing ionic radius from U to Am.[114]

A noteworthy phenomenon was observed in the series of solid terpy lanthanide(III) complexes $[MB(H_2O)_xCl^+][Cl^-]_2 \cdot 3H_2O$, namely, an inversion of the relation R_{M-N} between the M−N bond distances to the central and the lateral N atoms ($R_{M-N} = M-N_{central}/M-N_{lateral}$). As seen in Figure 8, the distances are $M-N_{lateral} < M-N_{central}$ for M = La to Sm and $M-N_{lateral} > M-N_{central}$ for M = Eu to Lu.[121] The trend was satisfactorily described by DFT calculations.[122] Figure 8 shows that the calculated relations between the $M-N_{lateral}$ and $M-N_{central}$ bond distances agree well with the experimental values, even if calculated absolute distances differ to some extent from the experiment.

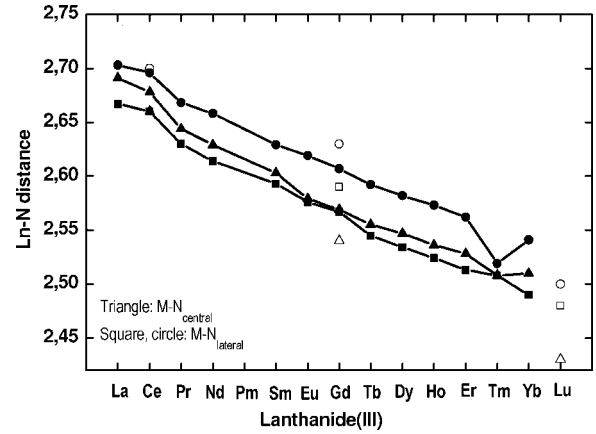


Figure 10. Bond distances between lanthanide(III) ions and nitrogen atoms in crystal complexes of TPTZ. Solid points are $[MB(H_2O)(NO_3)_3] \cdot 2EtOH$[126] {*136,139,140,143−145,148−154*}[T8]; open points are $[MB(H_2O)(NO_3)_3]$[127] with M = Ce {*138*}[T8], Gd {*147*}[T8], and Lu {*155*}[T8].

The cause of this effect is sought in a donor interaction of the central N atom and an acceptor interaction of the lateral N atoms with the M^{3+} ion. As an evidence, similar trends are said to be visible in the change of the M(III)/M(II) potential and the nitrogen radius (i.e., the difference between the M−N distance and the ionic radius of M^{3+}) with the atomic number.[56] However, not only is this evidence in a graphical form little convincing, but the inversion of the bonding distance is not unambiguously found in terpy complexes with another counteranion, namely, in nitrate complexes. It is true that strictly comparable data on nitrate-containing terpy complexes are available for only four Ln(III), but even so few values could give consistent results. This is not the case. An inversion somewhere between La(III) and Gd(III) is indicated by data on the complexes $[MB(H_2O)_3(NO_3)_2^+][NO_3^-]$[123] (M = La {*10*}[T8] and Gd {*42*}[T8]) and somewhere between Er(III) and Tm(III) by data on the complexes $[MB(H_2O)_3(NO_3)_3] \cdot B$[104] (M = Ho {*52*}[T8], Er {*54*}[T8], and Tm {*57*}[T8]). No uniform trend is indicated by data on the complexes $[MB(H_2O)(NO_3)_3]$ (M = Nd[104] {*28*}[T8], Eu[124] {*38*}[T8], Tb[124] {*45*}[T8], Tm[104] {*58*}[T8]). Finally, no trend to an inversion is shown by data on the complexes $[MB(H_2O)_2(NO_3)_2^+][NO_3^-]$[123] (M = Tb {*47*}[T8] and Lu {*67*}[T8]).

No tendency to an inversion is insinuated by data on the complexes of 2,6-bis(5-methyl-1,2,4-triazol-3-yl)pyridine[125] ($[MB(H_2O)(NO_3)_3]$ with M = Nd {*4*}[T8], Sm {*5*}[T8], Tb {*6*}[T8], and Ho {*7*}[T8]), 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine[79] (Figure 9), and TPTZ,[126,127] (Figure 10). In the last two cases it is in accord with prediction by DFT calculations.[122] By the way, Figure 9 compares data on the aqua and triaqua complexes of 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine with La(III) to Sm(III) and demonstrates the sensitivity of the M−N bonding distances and the relations between them to the composition of the complexes. See in Figure 10 also an illustration of how markedly different data from two sources can be even if they are given for practically the same complexes ($[MB(H_2O)(NO_3)_3] \cdot 2EtOH$[126] and $[MB(H_2O)(NO_3)_3]$[127]).

In contrast to tridentate ligands, data on nitrate complexes of the tetradentate, purely heterocyclic ligand 6,6′-bis(5,6-diethyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl[44] indicate an inversion of R_{M-N} at Nd(III). Available data on complexes of the tetradentate tris(2-pyridylmethyl)amine ligand reveal no

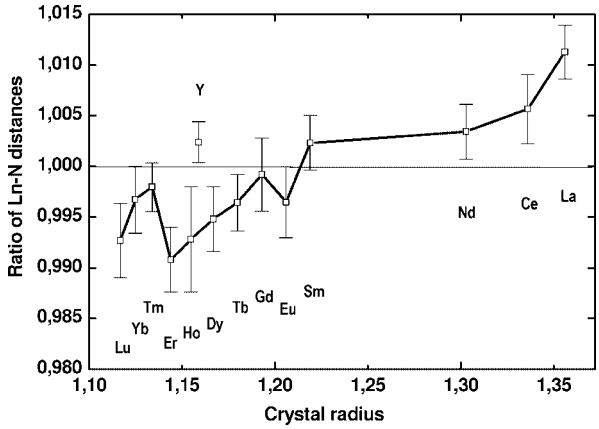


Figure 11. Data from Figure 8 on terpy chloride complexes plotted as a dependence of the $M-N_{central}/M-N_{lateral}$ distance ratio on the crystal radius of the central lantanhide(III) ion. Open points are experimental values for $[TmB(H_2O)_4Cl^{2+}][Cl^-]_2 \cdot 2H_2O$ and $[MB(H_2O)_xCl^{2+}][Cl^-]_2 \cdot 3H_2O$ with $x = 4$ to 5 for other M {*12,15,30,37,39,44,48,50,53,56,59,60,64,71*}[T8].

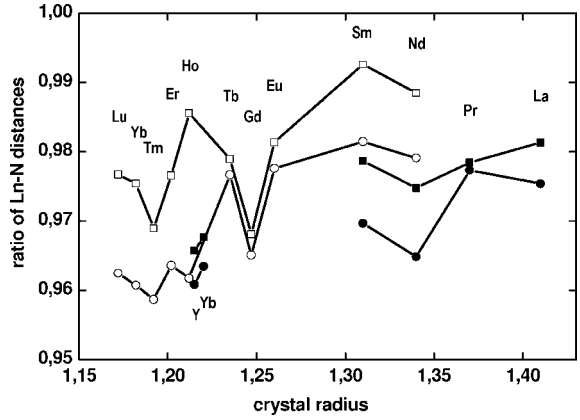


Figure 12. Data from Figure 9 on complexes of 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine plotted as a dependence of the $M-N_{central}/M-N_{lateral}$ distance ratio on the crystal radius of the central lanthanide(III) ion: (□) $M-N_{central}/M-N_{lateral(1)}$; (○) $M-N_{central}/M-N_{lateral(2)}$. Solid points are $[MB(H_2O)(NO_3)_3]$ {*120−122,124,132*}[T8]; open points are $[MB(H_2O)_3(NO_3)_2^+][NO_3^-]$ with M = Nd {*123*}[T8] and Sm {*125*}[T8] and $[MB(H_2O)_2(NO_3)_2^+][NO_3^-]$ for other M {*126−131,133,134*}[T8].

inversion of R_{M-N} either in $[MBCl_3]$[89] (M = Eu {*164*}[T8], Tb[89] {*168*}[T8], and Lu[89] {*169*}[T8]) or in $[MB_2^{3+}][I^-]_3$[87] (M = La {*158*}[T8], Ce {*160*}[T8], Nd {*162*}[T8], and Lu {*170*}[T8]).

It was checked in this review whether more insight into the bond distance relations can be obtained in correlating R_{M-N} values with the radii of the central lanthanide ions. A clear increase of the R_{M-N} with the crystal radius is brought into view by data on terpy chloride complexes (see Figure 11), even if it is not strictly monotonous. A less clear picture is given by data on nitrate complexes of 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine (see Figure 12). It can be said, indeed with some imagination, that also in this case the general trend is an increase of R_{M-N} with the crystal radius. Also less clear is the picture given by data on TPTZ (Figure 13), where some increase of R_{M-N} with the crystal radius could be recognized between La(III) and Gd(III) but not in heavier Ln(III). A rather visible increase of the R_{M-N} with the crystal radius, at least in the region of light lanthanides, is exhibited in complexes of 6,6′-bis(5,6-diethyl-1,2,4-triazin-3-yl)-2,2′-bipyridyl.

It is obvious that the ionic radius of M^{3+} belongs to those factors that influence the bonding distances in planar

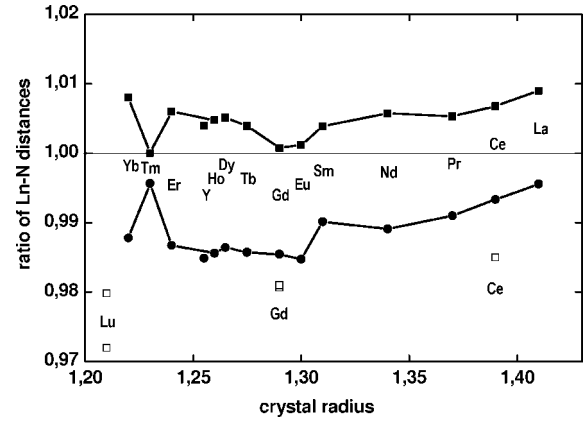


Figure 13. Data from Figure 10 on complexes of TPTZ plotted as a dependence of the $M-N_{central}/M-N_{lateral}$ distance ratio on the crystal radius of the central lantanhide(III) ion: (□) $M-N_{central}/M-N_{lateral(1)}$; (○) $M-N_{central}/M-N_{lateral(2)}$. Solid points are $[MB(H_2O)(NO_3)_3] \cdot 2EtOH$ {*136,139,140,143−145,148−154*}[T8]; open points are $[MB(H_2O)(NO_3)_3]$ with M = Ce {*138*}[T8], Gd {*147*}[T8], and Lu {*155*}[T8].

complexes of tridentate N-donors such as terpy and, less clearly, 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine and TPTZ. It is a possible explanation that with decreasing ionic radius the Ln^{3+} ions may become better accommodated in the cavity of the donor. That is, they can enter farther in the depth of the cavity and approach more closely the central nitrogen atom. These steric circumstances can be largely altered by the nature of further ligand bound to the central ion, such as inorganic anions. Their may act sterically, but they may as well influence those electrons of the central ion that are responsible for the formation of chemical bonds.

In one case, namely, in the complexation of heavier Ln(III) by 2,6-bis(1-methylbenzimidazol-2-yl)pyridine, it is even assumed that the accommodation of a smaller Ln^{3+} ion forces the cavity to shrink and evokes in this way a steric constraint.[55]

To predict relations between $M-N_{central}$ and $M-N_{lateral}$ bonding distances, quantum mechanics calculations of the distances in complexes of the type $[LnB^{3+}]$ in vacuum were performed. The central ions were La^{3+}, Eu^{3+}, and Lu^{3+}, and the ligands were terpy, TPTZ, 4-amino-2,6-di(2-pyridyl)-1,3,5-triazine, 2,6-di(2-pyridyl)pyrimidine, 2,6-di(2-benzimidazolyl)pyridine, and 2,6-bis(1,2,4-triazin-3-yl)pyridine. Longer $M-N_{central}$ bonding distances than $M-N_{lateral}$ were predicted for the La(III)−terpy complex, as well as for the complexes of all three Ln^{3+} with 2,6-di(2-benzimidazolyl)pyridine and 2,6-bis(1,2,4-triazin-3-yl)pyridine. In all other complexes, the predicted $M-N_{central}$ is shorter than the $M-N_{lateral}$.[56] Validity of the results of the calculations in solid crystals cannot be verified by assessing data in Table 8, because no M−N distances are available for simple complexes $[MB^{3+}]$. All studied 1:1 complexes contain additional ligands in the coordination sphere of the M^{3+} ion, such as MeOH, H_2O, NO_3^-, and Cl^-, which can influence the M−N distances to an extent not easily estimable.

Data on the $M-N_{central}/M-N_{lateral}$ distance ratio in An(III) complexes are limited to DPTP complex $[CmB_3^{3+}]$, which was studied by EXAFS, indeed not in the solid state but in a solution in TPH/1-octanol (7/3 v/v). The relation $M-N_{central} < M-N_{lateral}$ was found in Monte Carlo simulation of the EXAFS spectra, with the $Cm-N_{lateral}$ bonding distances being 2.57 and 2.59 Å and the $Cm-N_{central}$ distance being 2.52 Å.[78]

3.3.11. Application of N-Donors to An(III)/Ln(III) Separation

Applications of N-donors in a nuclear partitioning process, although a topic different from those dealt with in previous sections, should be at least shortly mentioned. Just general remarks can be made, because description of the process development work performed up to now would exceed the scope of this review. The reader can find more information in relevant sources.[10,11,97]

According to present concepts,[128,129] An(III) and Ln(III) will be simultaneously extracted from acidic high-level liquid radioactive waste by an O-donor (e.g., bidentate carboxamide[128] or phosphine oxide[129]). It cannot distinguish between An(III) and Ln(III), but it is able to extract An(III) and Ln(III) at the typical acidity of the waste, that is, 3−5 M HNO_3. Following the stripping of An(III) and Ln(III) into 0.01−0.5 M HNO_3, An(III) will be extracted selectively from the strip by a N-donor. The subsequent stripping of An(III) could be done with >1 M HNO_3 if the N-donor (e.g., terpy {*20*}^{T6} or TPTZ {*53*}^{T6}) is used in combination with BDA. An(III) extracted by a BTP as nitrates cannot be easily replaced from the organic phase by >1 M HNO_3 {*28*}^{T6} and could be stripped either at a low nitrate concentration by <0.1 M HNO_3 or by a hydrophilic complexing agent such as citric acid.

In a nuclear process, the selective extraction of An(III) requires conditions under which in each stage of an extractor >50% An(III) is transferred into the organic phase and >50% Ln(III) remains in the aqueous phase. This can be attained by the selection of the extractant, diluent, and coextracted anion and by adjustment of suitable concentrations of these components and acid (see, for example, {*9,10,14,18−20,27−34,47−58*}^{T6}).

The choice of the optimum extractant is not unambiguous. None of the studied extractants possesses all of the desired properties, such as high separation and extraction efficiency, high chemical and radiation stability, fast reaction kinetics, good solubility in solvents suitable for a nuclear process, and easy accessibility. Thus, a compromise must be found, corresponding to the desirability of individual criteria. Further development is concentrated on improving the stability of molecules consisting of 2-pyridyl and 1,2,4-triazin-3-yl rings and less on search for new constituents of the extractant molecule. Possibilities of accelerating the extraction rate seem to merit more attention.

4. Abbreviations and Symbols

Methods and Variables

DFT	density functional theory
D_M, D_B	distribution ratio of the element M and the N-donor B, defined as the ratio of the sum of the concentrations of M and B in different forms, that is, $[B]_{org,tot}/[B]_{aq,tot}$ and $[M]_{org,tot}/[M]_{aq,tot}$
K_d	partition coefficient of B, defined as the ratio of the concentrations of a monomeric species of B, that is, $[B_{mono}]_{org}/[B_{mono}]_{aq}$

Solvents

DMF,	dimethylformamide
DMSO	dimethyl sulfoxide
MeCN	acetonitrile
MeOH	methanol
EtOH	ethanol
PrOH	propanol
Me_2CO,	acetone
MiBK	4-methyl-2-pentanone (methyl isobutylketone)
PrC	propylene carbonate
TCE	1,1,2,2-terachloroethane
TPH	hydrogenated "tetrapropylene", that is, highly branched dodecane

Complexants, Parts of Molecules

BDA	2-bromodecanoic acid
BHA	2-bromohexanoic acid
BTP	general acronym for bis-triazinyl-pyridines
DMTP	2,6-bis(5,6-dimethyl-1,2,4-triazin-3-yl)pyridine
DETP	2,6-bis(5,6-diethyl-1,2,4-triazin-3-yl)pyridine
DPTP	2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine
DiPTP	2,6-bis(5,6-diisopropyl-1,2,4-triazin-3-yl)pyridine
DiBTP	2,6-bis(5,6-diisobutyl-1,2,4-triazin-3-yl)pyridine
DNNS	dinonylnaphthalenesulfonic acid
py	pyridine
bipy	2,2′-bipyridyl
phen	1,10-phenanthroline
terpy	2,2′:6′,2″-terpyridyl
triflate	trifluoromethylsulfonate
TPTZ	2,4,6-tri(2-pyridyl)-1,3,5-triazine
Me	methyl
Et	ethyl
Pr	propyl
Bu	butyl
Ph	phenyl

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