3310 *Inorg. Chem.* **1998,** *37,* 3310−3315

Molecular Mechanics Calculations and the Metal Ion Selective Extraction of Lanthanoids

Peter Comba,[§] Karsten Gloe,[‡] Katsutoshi Inoue,[†] Torsten Krüger,[‡] Holger Stephan,[‡] and Kazuharu Yoshizuka*,[†]

Department of Applied Chemistry, Saga University, Honjyo 1, Saga 840, Japan,
Institut für Anorganische Chemie, Technische Universität, Dresden, Mommsenstrasse 6,
D-01062 Dresden, Germany, and Anorganisch-Chemisches Institut, Universität Heidelberg,
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Received May 30, 1997

A molecular mechanics force field for lanthanoid complexes coordinated to organophosphate and aqua ligands is presented. The ligand−metal−ligand (L−M−L) bending interaction are modeled with 1,3-nonbonded interactions (point on a sphere approach) and a harmonic M−L stretching potential is used for the stretching modes. The force field parameters not yet available in the MOMEC force field were fitted to all relevant X-ray crystal structures available in the literature. There is good overall agreement between the observed and the calculated structural parameters. The calculations also indicate that a quantitative structure property relationship (QSPR) may be obtained, which relates the complexation strain energy difference between the lanthanoid cations and La(III) with their relative extractability. Thus, molecular mechanics is an efficient tool for the design of new organophosphate ligands with metal ion specific lanthanoid(III) extractability properties.

Introduction

Molecular mechanics is a routine tool in organic chemistry,[1] and the development of novel approaches to optimize transition metal ion coordination geometries and of extensive parametrization schemes has led to a situation, where many problems involving inorganic compounds may now be solved satisfactorily with the support of force field calculations.[2,3] Among these are the determination of structures in solution,[3a−c] the interpretation of stereo- and metal ion selectivities,[3d−i] and the prediction of spectroscopic[3j−m] and electron-transfer properties,[3c,n] and many of these applications have been reviewed extensively.[2,4] The design of metal ion selective ligands seemed to be an ideal task for molecular modeling, but there are a number of inherent problems that limit its applicability.[2] A few published reports of successful applications to predict selective metal ion complexation demonstrate the possibilities and limits of force field calculations in this area.[3e−i]

Force fields for some lanthanoid metal complexes with selected donor sets have been reported.[5−7] Generally, commercial separation and refining systems for lanthanoid metals use solvent extraction with bisalkyl hydrogenphosphates.[8,9] The aim of designing new organophosphorus-extracting ligands with high selectivity for specific lanthanoid metal ions involved the development of a corresponding force field. In this paper, we present parameters for lanthanoid metal complexes with O donor atoms including aqua and phosphate ligands. Moreover, we present a quantitative structure−property relationship (QSPR) between the complexation strain energy difference between the lanthanoid cations and La(III) and the extractability trends of lanthanoid(III) ions with three bisalkyl hydrogenphosphate ligands described in a previous paper,[10] i.e., bis(4-ethylcyclohexyl) hydrogenphosphate (D4ECHPA), bis(4-cyclohexylcyclohexyl) hydrogenphosphate (D4DCHPA), and bis(2-ethylhexyl) hydrogenphosphate (D2EHPA) (see Chart 1).

Experimental Section

The molecular mechanics calculations were performed with the strain energy minimization program MOMEC[11] and the corresponding force

---

* Corresponding author. Tel.: +81-952-28-8670 (direct). Fax: +81-952-28-8591 (office). E-mail: yosizuka@ccs.ce.saga-u.ac.jp.
[†] Saga University.
[‡] Technische Universität, Dresden.
[§] Universität Heidelberg.

(1) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.

(2) Comba, P.; Hambley, T. W. *Molecular Modeling of Inorganic Compounds*; VCH: Weinheim, 1995.

(3) (a) Comba, P. *Commun. Inorg. Chem.* **1994**, *16*, 133. (b) Comba, P. In *Fundamental Principles of Molecular Modeling*; Gans, W., Amann, A., Boeyens, J. C. A., Eds.; Plenum Press: New York, 1996; p 167. (c) Comba, P.; Sickmüller, A. *Angew. Chem.* **1997**, *109*, 2089. (d) Bernhardt, P. V.; Comba, P.; Gyr, T.; Várnagy, K. *Inorg. Chem.* **1992**, *31*, 1220. (e) Hay, B. P.; Rustad, J. R.; Hostetler, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 11158. (f) Hay, B. P.; Rustad, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 6316. (g) Hay, B. P.; Zhang, D.; Rustad, J. R. *Inorg. Chem.* **1996**, *35*, 2650. (h) Comba, P.; Nuber, B.; Ramlow, A. *J. Chem. Soc., Dalton Trans.* **1997**, 347. (i) Comba, P.; Fath, A.; Kühner, A.; Nuber, B. *J. Chem. Soc., Dalton Trans.* **1997**, 1889. (j) Bernhardt, P. V.; Comba, P.; Hambley, T. W.; Massoud, S. S.; Stebler, S. *Inorg. Chem.* **1992**, *31*, 2644. (k) Bernhardt, P. V.; Comba, P. *Inorg. Chem.* **1993**, *32*, 2798. (l) Comba, P. *Inorg. Chem.* **1994**, *33*, 4577. (m) Comba, P.; Hambley, T. W.; Hitchman, M. A.; Stratemeier, H. *Inorg. Chem.* **1995**, *34*, 3903. (n) Comba, P., Sickmüller, A. *Inorg. Chem.* **1997**, *36*, 4500.

(4) (a) Hancock, R. D. *Prog. Inorg. Chem.* **1989**, *37*, 187. (b) Comba, P. *Coord. Chem. Rev.* **1993**, *123*, 1. (c) Hay, B. P. *Coord. Chem. Rev.* **1993**, *126*, 177.

(5) Reichert, D. E.; Hancock, R. D.; Welch, M. J. *Inorg. Chem.* **1996**, *35*, 7013.

(6) Cundari, T. R.; Moody, E. W.; Sommerer, S. O. *Inorg. Chem.* **1995**, *34*, 5989.

(7) Hay, B. P. *Inorg. Chem.* **1991**, *30*, 2876.

(8) Coleman, C. F.; Roddy, J. W. *Solvent Extr. Rev.* **1971**, *1*, 63.

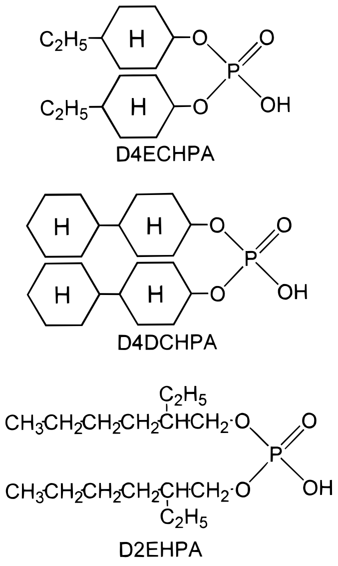
(9) Inoue, K.; Nakashio, F. *Kagaku Kogaku* **1982**, *46*, 164.

(10) Yoshizuka, K.; Kosaka, H.; Shinohara, T.; Ohto, K.; Inoue, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 589.

(11) Comba, P.; Hambley, T. W.; Lauer, G.; Okon, N. *MOMEC: A Molecular Modeling Package for Inorganic Compounds*; Lauer & Okon: Heidelberg, Germany, 1995. E-mail: CVS-HD@T-ONLINE.DE.

S0020-1669(97)00673-3 CCC: $15.00

Chart 1. Chemical Structures of D4ECHPA, D4DCHPA, and D2EHPA



field.[12] The functional forms and the parameters for the organic backbone of the ligands are described elsewhere.[12] A harmonic M−L stretching potential is used for the metal−donor interaction. The angular geometry around the metal center is modeled by interligand nonbonded interactions, and torsional potentials as well as nonbonded interactions involving the metal center are neglected.[2,11,12]

Input coordinates were obtained from the Cambridge Crystallographic Data Centre (CCDC) or produced with the graphics package HyperChem[13] which is interfaced with MOMEC. Initial values for the strain-free M−L distances and the corresponding force constants were taken from the literature[6,7] and then adjusted to obtain good agreement between the computed and the available X-ray structural data. The force field for the lanthanoid series of organophosphato complexes is based on 37 published structures and that for the aqua complexes on 38 published structures. More significantly, we use a single set of force field parameters for the two types of coordination sites of the nonaaqua ions (prismatic and cap, see below) which have considerably different M−O distances (difference of ca. 0.1 Å, ca. 4%, see Table 6, below). The final differences between observed and computed bond distances are ≤0.02 Å, and those for valence angles are ≤3°. The structures of the metal-free ligand molecules were also computed with PM3 using MOPAC93[14] (convergence criteria for GNORM = 0.01 and SCFRT = 0.00001).

Results and Discussion

Force Field Parameters for Lanthanoid Metal Complexes. The complete list of metal-independent force field parameters used for the lanthanoid metal complexes are given in Tables 1−4 and the metal-dependent force field parameters are presented in Table 5. The force field is based on modeling the angular geometry by 1,3-nonbonded interactions. A single set for the parameters for the stretching potentials for each of the two types of donors was used, i.e. the prismatic (P) and cap (C) positions (see Figure 1) were parametrized identically. Therefore, no constraint is imposed on the coordination geometry.

Table 1. Metal-Independent Bond Length Parameters

bond type[a]	k_r [mdyn Å^{-1}]	r_0 [Å]
C−C[b]	5.00	1.50
C−H[b]	5.00	0.97
O−H[b]	7.92	1.42
C−O(P)	5.00	0.91
P−O(H)	3.20	1.67
P−O(C)	3.20	1.69
P=O	7.30	1.45

[a] A symbol in brackets indicates a substituent of O. [b] Reference 12.

Table 2. Metal-Independent Valence Angle Parameters

angle type[a]	k_θ [mdyn rad^{-1}]	θ_0 [rad]
C−C−C[b]	0.45	1.91
C−C−H[b]	0.36	1.91
H−O−H[b]	0.32	1.90
O−C−H	0.49	1.91
O(C)−P=O	1.39	2.00
O(H)−P=O	0.62	2.01
O(C)−P−O(C)	0.62	1.72
O(C)−P−O(H)	0.62	1.76
P−O−C	1.39	2.07
P−O−H	0.62	2.04

[a] A symbol in brackets indicates a substituent of O. [b] Reference 12.

Table 3. Metal-Independent Torsion Angle Parameters

torsion type[a]	k_ϕ [mdyn rad^{-1}]	*m*	ϕ_0 [rad]
−C−C−[b]	0.002	3	0.00
−C−O−	0.080	3	0.05
−C−P−	0.072	3	0.00
−O(H)−P−	0.052	3	0.64
−O(C)−P−	0.052	3	0.39
−O=P−	0.052	3	0.39

[a] Symbols in brackets indicate substituents of O; ** indicate any atom. [b] Reference 12.

Table 4. Metal-Independent Nonbonded Interaction Parameters[a]

atom	r_{vdW} [Å]	ϵ [−]
C	1.90	0.044
H	1.44	0.024
O	1.70	0.055
P	2.10	0.146

[a] Reference 12.

Coordination of a ligand to a metal cation leads to some electron redistribution. Therefore, the bonding in metal-free and in coordinated ligands is slightly different, and consequently, the parametrization schemes may need to be different.[2] In a recent study we have shown, however, that the differences are rather small and generally only dependent on the charge and not the type of metal ion.[12c] Also, the metal−donor bonds to lanthanoid metals are dominated by electrostatic interactions. Thus, a common parameter set for the metal-free ligands and those coordinated to any lanthanoid(III) cation is a reasonable approach. The parametrization of the metal-free ligands has been tested with semiempirical MO calculations. Figure 2 shows the RMS overlay of the structures of the three metal-free bisalkyl hydrogenphosphate ligands, D4ECHPA, D4DCHPA, and D2EHPA, calculated by MOMEC and by PM3. The good agreement of the structures obtained by the MO calculations and those using our force field indicates that the metal-independent parameters are of good quality.

A plot of the force field parameters r_0 and k_r of the aqua ions vs the atomic number of the lanthanoid metal (see Figure

---

(12) (a) Bernhardt, P. V.; Comba, P. *Inorg. Chem.* **1992**, *31*, 2638. (b) Comba, P.; Hambley, T. W., Ströhle, M. *Helv. Chim. Acta* **1995**, *78*, 2042. (c) Bol, J. E.; Buning, C.; Comba, P.; Reedijk, J.; Ströhle, M., *J. Comput. Chem.* **1998**, *19*, 512.

(13) HyperChem Release 4.5, Serial No. 545-10001393, Hypercube, Inc.: Waterloo, Ontario, Canada 1995.

(14) Stewart, J. J. P. *MOPAC93: A Molecular Orbital Package*; JCPE P081; Stewart Computational Chemistry: Colorado Springs, CO, 1993.

Table 5. Metal-Dependent Parameters for Aqua and Phosphato Complexes

		aqua complex		phosphato complex		
lanthanoid(III)	atomic number	k_r [mdyn Å^{-1}]	r_0 [Å]	k_r [mdyn Å^{-1}]	r_0 [Å]	r_{vdW}^{a} [Å]
La	57	0.082	2.409	0.049	2.455	1.22
Ce	58	0.085	2.370	[0.053]^{b}	[2.410]^{b}	1.20
Pr	59	0.087	2.345	0.056	2.373	1.18
Nd	60	0.090	2.320	0.058	2.335	1.16
Pm	61	[0.092]^{b}	[2.289]^{b}	[0.062]^{b}	[2.319]^{b}	1.15
Sm	62	0.095	2.258	0.064	2.289	1.13
Eu	63	0.096	2.245	0.067	2.270	1.12
Gd	64	0.097	2.226	0.069	2.250	1.11
Tb	65	0.098	2.210	[0.070]^{b}	[2.231]^{b}	1.10
Dy	66	0.099	2.195	0.072	2.208	1.08
Ho	67	0.100	2.178	[0.073]^{b}	[2.181]^{b}	1.07
Y	67.6^{c}	[0.100]^{b}	[2.160]^{b}	[0.074]^{b}	[2.172]^{b}	1.07
Er	68	0.101	2.150	0.074	2.158	1.06
Tm	69	0.101	2.128	[0.075]^{b}	[2.136]^{b}	1.05
Yb	70	0.102	2.095	0.076	2.105	1.04
Lu	71	0.102	2.058	[0.077]^{b}	[2.078]^{b}	1.03

[a] References 24 and 43. [b] Parameters estimated from plots of k_r and r_0 vs atomic number. [c] The apparent atomic number of yttrium(III) is assumed to be 67.6 from the reported extraction equilibrium data.[15,16]

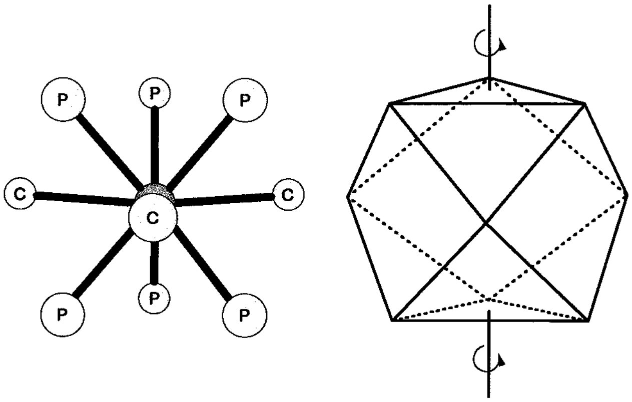


Figure 1. Geometry of an ideal tricapped trigonal prism.

3) revealed the expected trend, i.e. a decrease in r_0 and an increase in k_r with increasing atomic number.[15,16] The smooth curve allowed the interpolation of the parameters for the aqua ions of Pm(III) and Y(III), for which no X-ray data were available. Figure 4 is a plot of the observed M−O distances of the lanthanoid(III) organophosphato complexes, the ideal bond distance parameters r_0 and the van der Waals parameters of our force field (see Table 5), as a function of the atomic number of the lanthanoid. The smooth curve allowed the interpolation of the r_0 values in cases where no experimental structural data were available (Ce(III), Pm(III), Tb(III), Ho(III), Y(III), Tm(III), and Lu(III)). The force constants for these metal ions were also interpolated. All r_0 parameters are ca. 8% smaller than the observed M−O distances. The linear correlation between r_{vdW} and observed M−O distances is an indication that, as expected, there are no significant electronic contributions to the M−O distances.

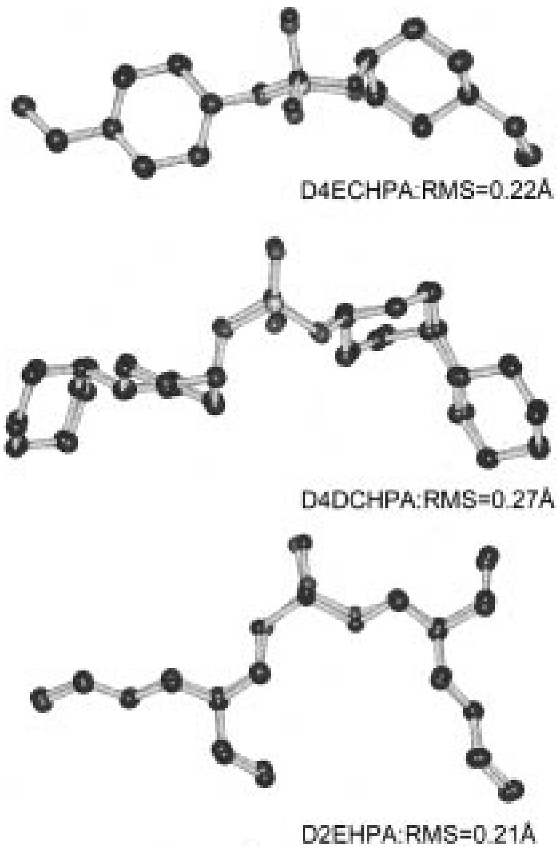


Figure 2. RMS overlay of computed MOMEC and PM3 structures of the metal-free ligands (hydrogen atoms omitted for clarity).

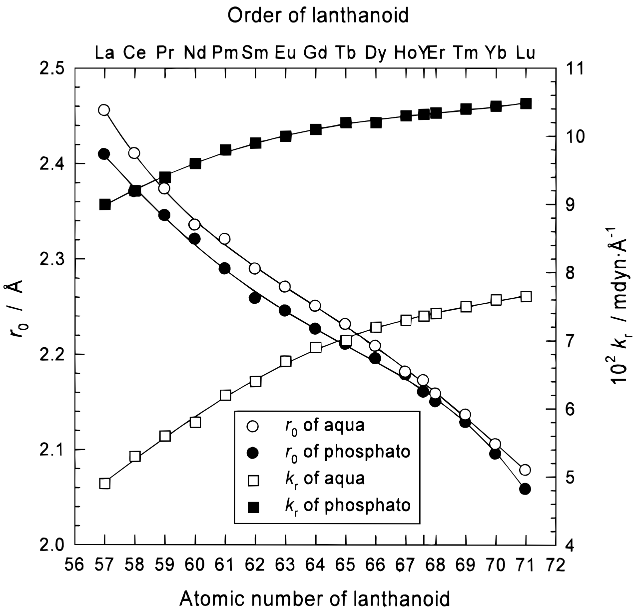


Figure 3. Plot of r_0 and k_r of aqua and phosphato complexes vs the atomic number of lanthanoids.

A comparison of observed and computed structural data of the lanthanoid(III) aqua and organophosphato complexes is given in Tables 6 and 7, respectively. As usual, there is some distortion of the crystal structures due to ion-pairing, hydrogen bonding, and crystal packing forces. Thus, the symmetry of the molecular cations in the crystal lattice is lower than that obtained by strain energy minimization, and it is only meaningful to compare averaged geometric parameters.[2,3] Generally, there is good agreement between the observed and computed structures.

Aqua Complexes. The structural properties of the aqua ions of lanthanoid(III) cations have been extensively studied, and X-ray data of 38 structures of nine-coordinate aqua complexes

---

(15) Peppard, D. F.; Mason, G. W.; Lewey, S. *J. Inorg. Nucl. Chem.* **1969**, *31*, 2271.

(16) Peppard, D. F.; Bloomquist, C. A. A.; Horwitz, E. P.; Lewey, S.; Mason, G. W. *J. Inorg. Nucl. Chem.* **1970**, *32*, 339.

Table 6. Comparison of Calculated and Observed Averaged M−O Bond Distances and O−M−O Valence Angles in Lanthanoid(III) Nonaaqua Complexes

	bond length [Å]			valence angle [deg]			
lanthanoid(III)[a]	M−O$_c$	M−O$_p$	M−O$_c$/M−O$_p$	O$_p$−M−O$_p$	O$_p$−M−O$_c$	U_{total} [kJ mol^{-1}]	ref
La(obsd)	2.615	2.516	1.039	76.0	69.3		19, 21, 24
La(calcd)[b]	2.619	2.513	1.042	75.6	69.4	−14.6	
La(calcd)[c]	2.615	2.515	1.040	75.9	69.0	−20.1	7
Pr(obsd)	2.590	2.470	1.047	75.6	69.3		18, 24
Pr(calcd)[b]	2.584	2.470	1.046	75.3	69.3	−11.3	
Pr(calcd)[c]	2.550	2.530	1.008	72.5	70.0	−10.0	7
Nd(obsd)	2.570	2.459	1.045	75.4	69.3		20, 21, 24
Nd(calcd)[b]	2.574	2.456	1.048	75.4	69.3	−9.8	
Nd(calcd)[c]	2.575	2.455	1.049	77.4	68.9	−13.4	7
Sm(obsd)	2.550	2.420	1.052	75.3	69.4		23, 24
Sm(calcd)[b]	2.548	2.421	1.052	75.7	69.2	−5.3	
Sm(calcd)[c]	2.520	2.500	1.009	72.6	70.0	−2.7	7
Gd(obsd)	2.399	2.539	1.058	75.3	69.4		19, 21, 24
Gd(calcd)[b]	2.402	2.529	1.053	75.8	69.2	−2.2	
Gd(calcd)[c]	2.413	2.547	1.056	77.6	68.8	−4.9	7
Ho(obsd)	2.516	2.372	1.059	75.3	69.4		17, 20, 24
Ho(calcd)[b]	2.510	2.376	1.056	76.0	69.2	2.8	
Ho(calcd)[c]	2.527	2.380	1.062	77.8	68.7	4.1	7
Yb(obsd)	2.520	2.320	1.087	75.5	69.3		18, 24
Yb(calcd)[b]	2.488	2.337	1.065	76.3	69.1	12.4	
Yb(calcd)[c]	2.460	2.430	1.012	72.9	70.0	24.6	7
Lu(obsd)	2.506	2.299	1.090	75.7	69.3		19, 21, 24
Lu(calcd)[b]	2.474	2.314	1.070	76.5	69.1	19.7	
Lu(calcd)[c]	2.505	2.341	1.070	78.1	68.7	18	7

[a] The tabulated parameters are averages over all relevant M−O bonds and cis O−M−O angles. [b] This work. [c] Reference 7.

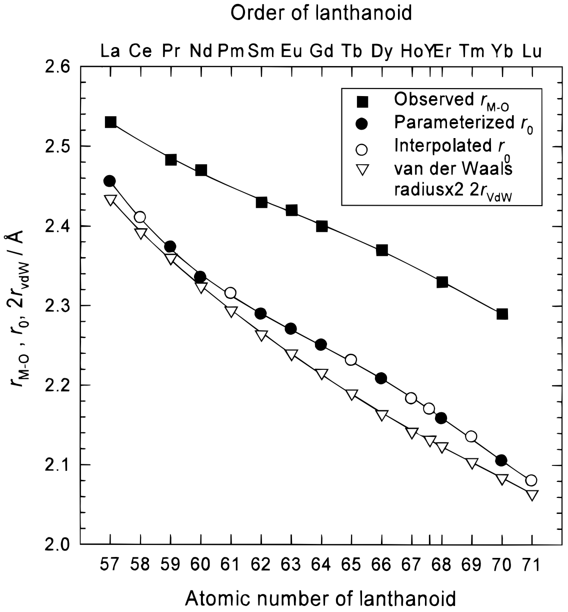


Figure 4. Plot of the metal donor distance r_{M-O}, the ideal metal−donor bond distance r_0, and the van der Waals radius of the metal ion r_{vdW} vs the atomic number of the lanthanoids for the phosphato complexes (the van der Waals radius has been doubled arbitrarily to fit the same scale).

are available.[17−24] These all have the stoichiometry $M(OH_2)_9\cdot X_3$ (X = counterion). MD simulations supported by solution spectroscopic analyses indicate, however, that there is a smooth change in coordination number (CN) from 9 (Nd(III)) to 8 (Yb(III)) along the series.[25] Compounds with EDTA-type (EDTA = ethylenediaminetetraacetic acid) ligands are generally nine-coordinate.[26,27] All the reported structures of the aqua ions have tricapped trigonal prismatic (TCTP) coordination polyhedra.[17−24] The only structures missing in the series of La(III) to Lu(III) are those of Pm(III) and Y(III). In the ideal TCTP geometry shown in Figure 1, there are six equivalent positions (O$_p$) at the vertexes of a regular trigonal prism and three equivalent positions (O$_c$) which cap the rectangular faces of this prism. Although the coordination geometry of all reported nonaaqua ions is similar, there are counterion-dependent structural differences that have been attributed to hydrogen bonding networks present in the crystal lattice.[18,19] The difference between the M−O$_p$ and M−O$_c$ bond distances has been attributed to interligand repulsion, leading to an elongation of the M−O$_c$ distances.[28] This trend is well reproduced in our calculations (see Table 6).

Organophosphato Complexes. X-ray data of 37 structures of lanthanoid(III) complexes with various organophosphates

---

(17) Hubbard, C. R.; Quicksall, C. O.; Jacobson, R. A. *Acta Crystallogr.* **1974**, *B30*, 2613.

(18) Albertsson, J.; Elding, I. *Acta Crystallogr.* **1977**, *B33*, 1460.

(19) Harrowfield, J. M.; Kepert, D. L.; Patrick, J. M.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 483.

(20) Pavia Santos, C. O.; Castellano, E. E.; Machado, L. C.; Vincentini, G. *Inorg. Chim. Acta* **1985**, *110*, 83.

(21) Chatterjee, A.; Maslen, E. N.; Watson, K. J. *Acta Crystallogr.* **1988**, *B44*, 381 and 386.

(22) Helmholz, L. *J. Am. Chem. Soc.* **1939**, *61*, 1544.

(23) Sikka, S. K. *Acta Crystallogr.* **1969**, *A25*, 621.

(24) Gerkin, R. E.; Repparte, W. J. *Acta Crystallogr.* **1984**, *C40*, 781.

(25) (a) Laurenczy, G.; Merbach, A. E. *Helv. Chim. Acta* **1988**, *71*, 1971. (b) Kowall, T.; Foglia, F.; Helm, L.; Merbach, A. E. *J. Phys. Chem.* **1995**, *99*, 13078. (c) Kowall, T.; Foglia, F.; Helm, L.; Merbach, A. E. *J. Am. Chem. Soc.* **1995**, *117*, 3790. (d) Kowall, T.; Foglia, F.; Helm, L.; Merbach, A. E. *Chem. Eur. J.* **1996**, *2*, 285.

(26) (a) Micskei, K.; Helm, L.; Brücher, E.; Merbach, A. E. *Inorg. Chem.* **1993**, *32*, 3844. (b) Powell, D. H.; Dhubhghaill, O. M. N.; Pubanz, D.; Helm, L.; Lebedev, Y. S.; Schlaepfer, W.; Merbach, A. E. *J. Am. Chem. Soc.* **1996**, *118*, 9333.

(27) (a) Geier, G.; Karlen, U. *Helv. Chim. Acta* **1971**, *54*, 1335. (b) Geier, G.; Joergensen, C. K. *Chem. Phys. Lett.* **1971**, *9*, 263.

(28) Keppert, D. L. *Inorganic Chemistry Concepts*; Springer, Berlin, 1980; Vol. 6.

Table 7. Comparison of Observed and Calculated M−O Bond Distances in Lanthanoid(III) Organophosphato Complexes

lanthanoid(III)	ligand[a]	average bond distance[b] [Å]	coordination number	ref
La(obsd)	L^1,L^2,L^3,L^4	2.53 ± 0.04	6, 8, 9	31−33, 35, 36, 38
La(calcd)		2.51 ± 0.03		
Pr(obsd)	L^3,L^4,L^5,L^6	2.48 ± 0.03	6, 8, 9, 10	31, 33, 36, 37, 39
Pr(calcd)		2.47 ± 0.04		
Nd(obsd)	L^3,L^4,L^6,L^7,L^8	2.47 ± 0.04	6, 8, 9	31, 33, 36, 37, 39
Nd(calcd)		2.45 ± 0.03		
Sm(obsd)	L^3,L^4,L^7,L^8	2.43 ± 0.02	6, 9	31, 33, 36
Sm(calcd)		2.43 ± 0.04		
Eu(obsd)	L^3,L^4	2.42 ± 0.04	6, 9	31, 36
Eu(calcd)		2.41 ± 0.03		
Gd(obsd)	L^3,L^4,L^7,L^8,L^9	2.41 ± 0.04	6, 9	31, 33−36
Gd(calcd)		2.40 ± 0.04		
Dy(obsd)	L^3,L^4,L^{10}	2.38 ± 0.04	8. 9	36, 39
Dy(calcd)		2.37 ± 0.03		
Er(obsd)	L^4,L^9	2.33 ± 0.04	8, 9	32, 35
Er(calcd)		2.34 ± 0.02		
Yb(obsd)	L^3,L^4,L^7,L^8,L^{11}	2.29 ± 0.03	6, 9	29, 31, 33, 37
Yb(calcd)		2.30 ± 0.03		

[a] L^1, bis(tetrakis-*O*-(diethylphosphoryl)-*p*-*tert*-butylcalix[4]arene; L^2, diisopropyl{1,2-bis(diethylcarbamoyl)-p-nitrobenzyl}phosphonate; L^3, dialkyl{1,2-bis(diethylcarbamoyl)ethyl}phosphonate; L^4, diaryl phosphine oxide; L^5, benzylhydroxylbis(dimethoxyl)phosphate; L^6, diisopropyl-α-hydroxyiminopropyl phosphate; L^7, diisopropyl{(*p*-tolylsulfonyl)methyl}phosphanate; L^8, diisopropyl{(*p*-tolylsulfinyl)methyl}phosphanate; L^9, 1-phosphono-1-carbamoyl-*n*-phosphono alkane; L^{10}, 6,6′-bis(diphenylphosphinomethyl)-2,2′-bipyridine-*N*,*N*′,*P*,*P*′-tetraoxide; L^{11}, tris(tetraphenylimido)diphosphate. [b] The tabulated structural parameters are averages over all relevant calculated or observed parameters.

have been published,[29−40] including (number of available structures in parentheses) La(6), Pr(5), Nd(5), Sm(2), Eu(2), Gd(5), Dy(4), Er(4), and Yb(4). The coordination numbers vary from 8 to 10 with water and counterions such as nitrates and chlorides as extra ligands. Most of the reported structures have CN = 9 and distorted TCTP coordination.[29−40] Figure 5 shows the overlay of the experimental[29,30] and the calculated lowest strain energy structure of a tris(tetraphenyl imidodiphosphato)-Yb(III) complex as an example for the quality of the structural predictions. Comparison of selected observed and calculated structural features for lanthanoid(III) organophosphato complexes are given in Table 7.

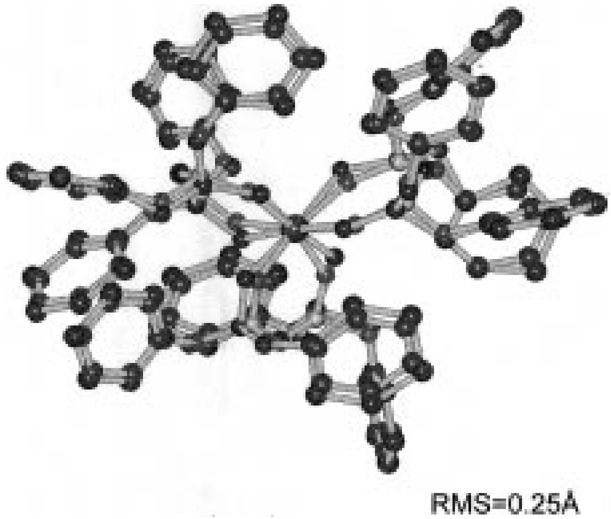


Figure 5. RMS overlay of the observed[30] and the computed structures of tris(tetraphenyl diphosphato)Yb(III) (hydrogen atoms omitted for clarity).

QSPR of Extractability Trends of Lanthanoid(III) Ions with Bisalkyl Hydrogenphosphates. In a previous publication[10] we proposed the structures of lanthanoid complexes coordinated to D4ECHPA, D4DCHPA, and D2EHPA (see Chart 1) from the stoichiometry of the species extracted to the organic phase. The structural model used in our strain energy minimization procedures is based on these observations and the fact that most lanthanide(III) complexes have CN = 9.

Figure 6 is a comparison of some calculated energy terms of the computed compounds with D4ECHPA, D4DCHPA, and D2EHPA as a function of the order of the metal ion. The torsional and valence angle deformation energies are the dominant strain energy terms. However, these angle deformation energies are not significantly dependent on the size of the metal ion. Thus, the terms which may be related to the metal ion selectivity are the van der Waals repulsion and the M−O stretching energies. The observed trend may be related to the lanthanoid contraction.[15,16]

QSPR's for estimating the strain energy contribution to the thermodynamics of complex formation have been proposed for transition metal complexes with polyamines and for lanthanoid complexes.[3e,41,42] For the lanthanoid(III) compounds studied here, the relation between the total strain energy and the complex formation can be expressed by

$$\begin{array}{ccccccccc} \mathrm{M(H_2O)_9}^{3+} & + & 6\mathrm{HR} & \rightleftarrows & \mathrm{M(HR_2)_3{\cdot}3H_2O} & + & 3\mathrm{H}^+ & + & 6\mathrm{H_2O} \\ U_{\mathrm{M}} & & 6U_{\mathrm{HR}} & & U_{\mathrm{Mcom}} & & 3U_{\mathrm{H}} & & 6U_{\mathrm{aq}} \end{array} \quad (1)$$

where U_i (i = M, HR, Mcom, H, and aq) are the relevant terms contributing to the total strain energy. Thus, the strain energy contribution to complex formation is given by

$$\Delta U_{\mathrm{M}} = U_{\mathrm{Mcom}} + 3U_{\mathrm{H}} + 6U_{\mathrm{aq}} - U_{\mathrm{M}} - 6U_{\mathrm{HR}} \quad (2)$$

Since energies obtained by force field calculations are relative energy terms, i.e., they depend on the type of compound and on the force field used, it is reasonable to consider strain energy differences, e.g. differences to La(III) as a reference. The relative

---

(29) Kulpe, S.; Seidel, I.; Szulzewsky, K.; Kretschmer, G. *Acta Crystallogr.* **1983**, *B38*, 2813.
(30) Herrmann, E.; Hoang, B. N.; Dreyer, R. *Z. Chem.* **1979**, *19*, 187.
(31) Chaozhou, N.; Changtao, Q. *Inorg. Chim. Acta* **1985**, *110*, L7.
(32) Kapoor, P. N.; Saraswati, R.; McMahon, I. J. *Inorg. Chim. Acta* **1985**, *110*, 63.
(33) Karthikeyan, S.; Paine, R. T.; Ryan, R. R. *Inorg. Chim. Acta* **1988**, *144*, 135.
(34) McCabe, D. J.; Duesler, E. N.; Paine, R. T. *Inorg. Chim. Acta* **1988**, *147*, 265.
(35) Karthikeyan, S.; Ryan, R. R.; Paine, R. T. *Inorg. Chem.* **1989**, *28*, 2783.
(36) Conary, G. S.; McCabe, D. J.; Meline, R. L.; Duesler, E. N.; Paine, R. T. *Inorg. Chim. Acta* **1993**, *203*, 11.
(37) Platt, A. W. G.; Simpson, D.; Fawcett, J.; Russell, D. R. *Inorg. Chim. Acta* **1994**, *223*, 43.
(38) Bligh, S. W. A.; Choi, N.; Hudson, H. R.; McGrath, C. M.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2335.
(39) Harrowfield, J. M.; Mocerino, M.; Peachey, B. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1996**, 1687.
(40) Gan, X.; Duesler, E. N.; Paine, R. T.; Smith, P. H. *Inorg. Chim. Acta* **1996**, *247*, 29.
(41) Comba, P.; Sickmüller, A. *Inorg. Chem.* **1997**, *36*, 4500.
(42) (a) Hancock, R. D.; McDougall, G. J.; Marsicano, F. *Inorg. Chem.* **1979**, *18*, 2847. (b) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875.
(43) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

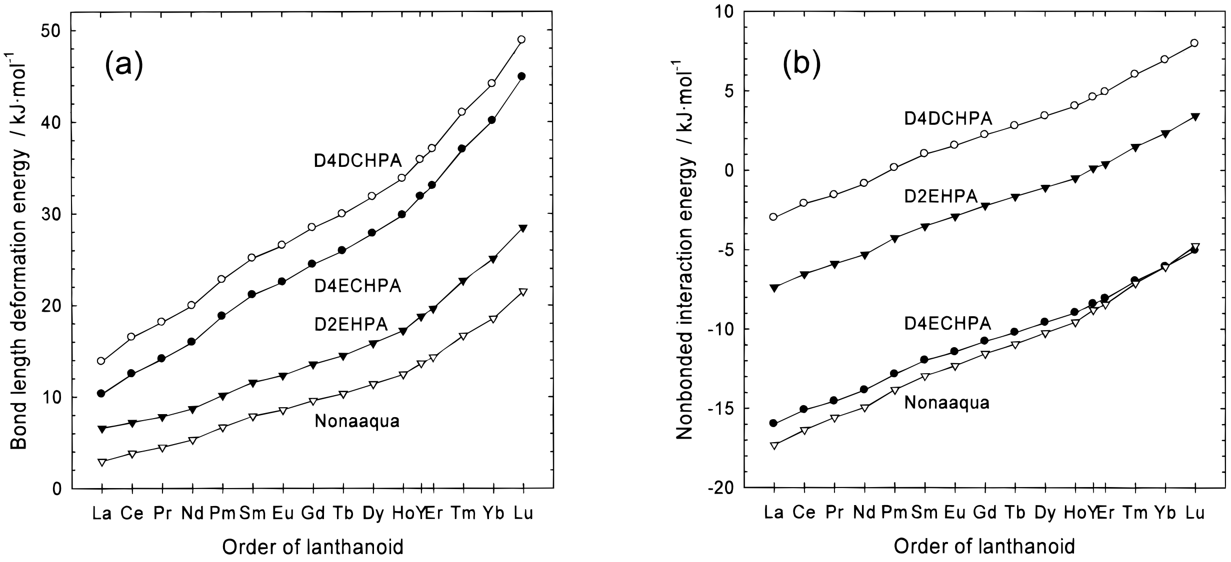


Figure 6. Bond length deformation and nonbonded interaction energies of M−O vs order of lanthanoid complexes; (a) bond length deformation and (b) nonbonded interaction.

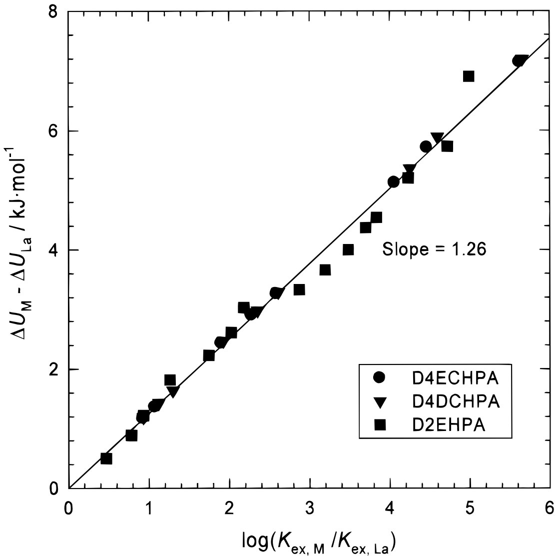


Figure 7. Plot of $\Delta U_M - \Delta U_{La}$ vs $\log(K_{ex,M}/K_{ex,La})$.[10]

strain energy with respect to that of the La(III) compounds is given by

$$\Delta U_M - \Delta U_{La} = (U_{Mcom} - U_{Lacom}) - (U_M - U_{La}) \quad (3)$$

From the extraction constant ($K_{ex,M}$), the following free energy relationship is obtained:

$$\Delta G_M = -RT \ln K_{ex,M} \quad (4)$$

From eqs 3 and 4, it follows that

$$\Delta U_M - \Delta U_{La} = \alpha \log(K_{ex,M}/K_{ex,La}) \quad (5)$$

where α is the apparent QSPR constant of above relationship. At 298 K ($RT = 2.48$ kJ mol^{-1}), and with the conversion factor of ln to log of 1/2.30, α is 1.08.

A plot of ($\Delta U_M - \Delta U_{La}$) vs $\log(K_{ex,M}/K_{ex,La})$ for the three extracting ligands considered here[10] (see Figure 7) revealed a good linear relationship with a slope (α) of 1.26. The small but significant deviation from the theoretical value (1.26 vs 1.08) may be due in part to the neglect of entropy, ion pairing, and solvation in eq 5. The high degree of linearity suggests that the neglected terms are either constant or linearly dependent on the strain energy over the whole series of compounds considered here (for a detailed discussion of these effects, see ref 41). A similar slope (α = 1.15) has been obtained for the complexation of transition metal ions with polyamine ligands.[42] The QSPR also allows for designing new extractants with structural properties similar to those of the three ligands described here, with improved separation properties: the log of the relative extractabilities of the complexes correlates with the relative strain energies with a slope of ca. 1.25. That is, as expected, increasing bulk of the substituents of the organophosphato ligands will lead to an increasing selectivity, and this may be predicted quantitatively with the force field discussed here.

Nomenclature

ΔG_M	free energy difference in complex formation [kJ mol^{-1}]
$K_{ex,M}$	extraction constant [−]
k_T	force constant for bond length deformation [mdyn Å^{-1}]
k_ϕ	force constant for torsion angle deformation [mdyn rad^{-1}]
k_θ	force constant for valence angle deformation [mdyn rad^{-1}]
m	periodicity [−]
R	gas constant [kJ mol^{-1} K^{-1}]
r_{M-O}	observed bond length of M−O [Å]
r_0	strain-free bond length [Å]
r_{vdW}	van der Waals radius [Å]
T	temperature [K]
U_i	strain energy of species i [kJ mol^{-1}]
U_{total}	total strain energy [kJ mol^{-1}]
ΔU_M	energy difference in complex formation [kJ mol^{-1}]
α	apparent QSPR constant [−]
ϵ	hardness parameter [−]
ϕ_0	strain-free valence angle [rad]
θ_0	strain-free torsion angle [rad]

Acknowledgment. K.Y. gratefully acknowledges the financial support for a visit for foreign academic personnel to Germany from the DAAD to the Dresden University of Technology and the University of Heidelberg. P.C. and K.G. are grateful for financial support by the Deutsche Forschungsgemeinschaft (DFG). K.Y. and K.I. acknowledge financial support by a Grant-in-Aid for Scientific Research (B) (09450293) from the Ministry of Education, Science, Sports and Culture of Japan.

IC970673R