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Some Remarks on the Periodical Change of the Stability Constants of the Lanthanide Complexes

Marek Majdan

Institute of Chemistry, UMCS, PL-20-031 Lublin, Poland

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The correlations between the values of the $\lg K$ (K = stability constant of the lanthanide complex) and the reciprocal of the ionic radius $1/r$ or the sum of the ionization potentials $\sum_1^3 I$ for the lanthanide ions were reviewed for different ligands. A straight-line relationship $(\lg K' - \lg K)/\lg K'$ vs. $(1/r' - 1/r)/(1/r')$ or vs. $(\sum_1^3 I' - \sum_1^3 I)/\sum_1^3 I'$ was found within the tetrads La—Nd, Gd—Ho, and Er—Lu.

(Keywords: Lanthanide complexes; Ionic radius; Ionization potential; Double-double effect)

Bemerkungen zum periodischen Wechsel der Stabilitätskonstanten von Lanthaniden-Komplexen

Es wurde eine Übersicht der Korrelationen zwischen den Werten von $\log K$ (K = Stabilitätskonstante der Lanthanidenkomplexe) und den reziproken Ionenradien $1/r$ oder der Summe der Ionisierungspotentiale $\sum_1^3 I$ für die Lanthanidenionen für verschiedene Liganden gegeben. Dabei wurde eine lineare Korrelation für $(\lg K' - \lg K)/\lg K'$ gegen $(1/r' - 1/r)/(1/r)$ oder gegen $(\sum_1^3 I' - \sum_1^3 I)/\sum_1^3 I'$ innerhalb der Tetraden La—Nd, Gd—Ho und Er—Lu aufgefunden.

Introduction

1966 and 1971 *Fidelis* and *Siekierski* [1, 2] reported about the periodical change of the stability constants of the lanthanide complexes. This change, which they called double-double effect, relies on the division of the lanthanide series on subgroups which refer to the electronic configurations: f^3, f^4, f^7, f^{10}, f^{11}. The configuration f^7 divides the whole series on two subgroups f^0–f^7 and f^7–f^{14}. The configurations f^3, f^4 and f^{10}, f^{11} divide each of the subgroups into two parts. Within these parts changes of the properties of the lanthanides such as ionic radius, thermodynamical functions of the complexations and crystallization, unit cell dimensions of the compounds, and *Racah* parameters [3–8] remain the same. The whole series is divided into four parts named tetrads [9] but the division is more pronounced for the light lanthanides than for the heavy ones. Recently *Sinha* [10] classified the chemical properties of the lanthanides taking the quantum number of the electronic states, L, as the criterion of classification. He received straight-line relationships P_i vs. L (where P_i is the chemical property of the lanthanide) within the tetrads La—Nd, Pm—Eu, Gd—Ho, and Er—Lu. It seems, however, that a too small number of ligands was reviewed and that the conclusions of *Sinha* are premature. In this paper the following relationships were reviewed for different ligands:

$$\frac{(\lg K' - \lg K)}{\lg K'} = b* \frac{(1/r' - 1/r)}{1/r'} + a \tag{1}$$

$$\frac{(\lg K' - \lg K)}{\lg K'} = b* \frac{(\sum_1^3 I' - \sum_1^3 I)}{\sum_1^3 I'} + a \tag{2}$$

(where K' refers to the stability constant of the complex of the first lanthanide of the tetrad, r is the ionic radius of the lanthanide ion [11], and $\sum\limits_1^3 I$ is the sum of the ionization potentials of the lanthanide ions [12]).

The bonding in the lanthanide complexes is mainly ionic and the attraction central ion—ligand is, as we know, determined by the function $1/r$. It was established earlier [13] that the value of the lanthanide ionic radius changes periodically with the atomic number. Thus, if the change of the value $\lg K$ is also periodical (Fig. 1), we should receive the straight-line relationship $\lg K$ vs. $1/r$ within the tetrads.

The f-electron properties of the lanthanides are emphasized also very good by the change of the ionization potentials. We can notice the breaks of the plots: $\sum_1^3 I$ vs. atomic number Z for the specified electron configurations (Fig. 2). Therefore in these cases, when we expect some part covalency [uncharged ligands] in bond metal-ligand, the ionization potential should be taken as the criterion of the evaluation of the stability constants changes in the lanthanide series.

Results and Discussion

The correlation coefficients p^2 and the parameters of the equations describing the correlation between the stability constants of the lanthanide complexes and the ionization potentials or the reciprocal of the ionic

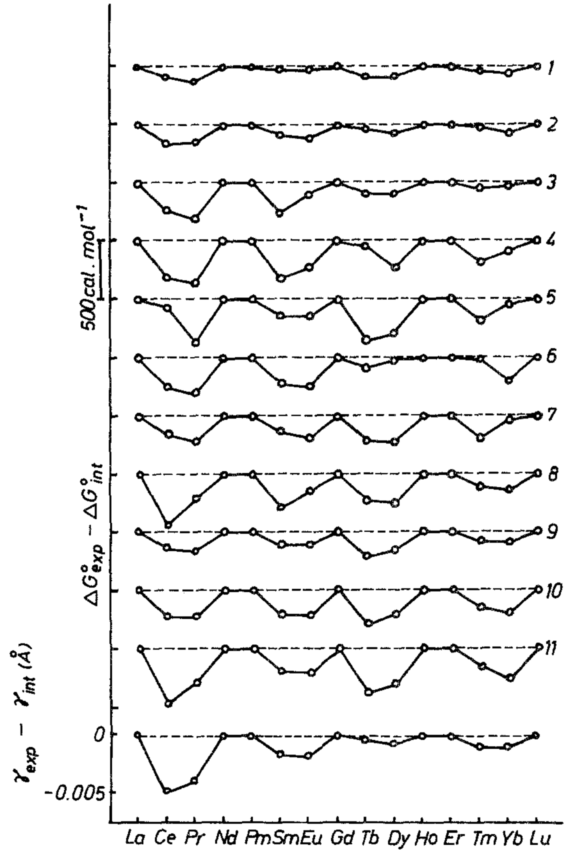

Fig. 1. The free energy of the complexation and the ionic radius as a function of the lanthanide and the ligand according to *Siekierski* [13] (the bottom part of the figure refers to the changes of the ionic radius expressed as $r_{\mathrm{exp.}} - r_{\mathrm{int.}}$, where subscripts exp. and int. mean experimental and interpolated values of the ionic radii). *1* Lactic acid; *2* α-hydroxyisobutyric acid; *3* 1-hydroxycyclopentanecarboxylic acid; *4* picolinic acid; *5* dipicolinic acid; *6* N-Hydroxyethylenediaminetriacetic acid; *7* Ethylenediaminetetraacetic acid; *8* Diethylenetriaminepentaacetic acid; *9* Tributylphosphate; *10* Di(2-ethylhexyl)phosphoric acid; *11* 2-Ethylhexylphenylphosphoric acid

radius are given in Table 1. The tetrad Pm—Gd was omitted due to lack of experimental data for Pm. It is easy to notice that in most cases a good correlation between the stability constant values and $1/r$ or $\sum_1^3 I$ was obtained. The graphical illustration of this correlation is shown on Figs. 3 and 4. In the case of the light lanthanides the values of the stability constants are determined more by $1/r$ than by I (see Table 1; compare the correlation coefficients for Eqs. 1 and 2) for all ligands. It seems that the bonding in the light lanthanide complexes possesses more ionic character than in the heavy ones. The shrinkage of the ionic radius causes the increase of the polarizing power of the lanthanide ion and thus the increase of the ability to the formation of covalent bonds with ligands. Therefore the correlation in the fourth tetrad Er—Lu is determined by the changes of the ionic radius for strongly charged ligands (*EDTA*, *PDTA*, *DBTA*, *DPTA*, *DCTA*) and by the changes of the ionization potentials for uncharged or weakly charged ligands (8-hydroxy-5,7-diiodoquinoline,2,4-dihydroxybenzaldehyde,hydroxyiminoacetone). There is lack of correlation in some cases (α,β,β'-trihydroxyisobutyrate, methoxyacetate) but it results rather from errors in the experimental data.

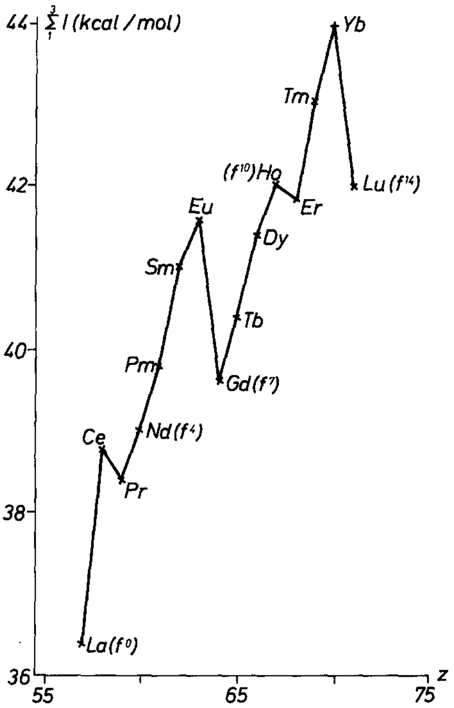

Fig. 2. The ionization potential $\sum_1^3 I$ as a function of the lanthanide

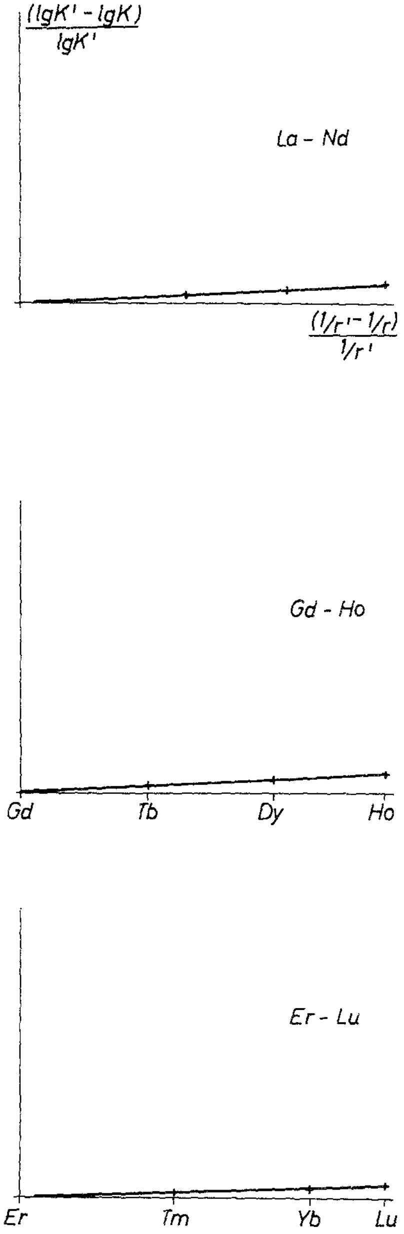

Fig. 3. The increase of the stability constants as a function of the reciprocal of the ionic radius for the lanthanide—*EDTA* complexes

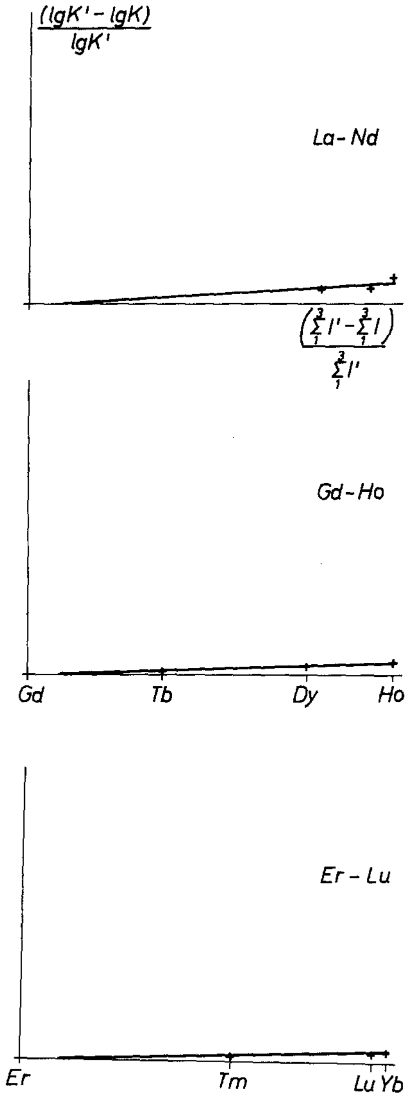

Fig. 4. The increase of the stability constants as a function of the ionization potential $\sum I$ for the lanthanide—8-hydroxy-5,7-diiodoquinoline complexes

Table 1. *Correlation coefficients p^2 and parameters of Eqs. 1 and 2*

Tetrad	Ligand					
	Eq. (1)			Eq. (2)		
	a	*b*	p^2	*a*	*b*	p^2
EDTA						
La—Nd	0.0030	1.45	0.995	0.0012	0.78	0.845
Gd—Ho	0.0036	1.70	0.990	0.0003	1.11	0.994
Er—Lu	0.0012	1.97	0.986	0.0003	0.80	0.940
PDTA						
La—Nd	−0.0026	1.34	0.993	0.0000	0.69	0.800
Gd—Ho	0.0017	1.48	0.995	0.0030	0.82	0.988
Er—Lu	0.0013	1.84	0.984	0.0005	0.75	0.940
DBTA						
La—Nd	0.0011	1.42	0.998	0.0007	0.79	0.881
Gd—Ho	0.0014	1.64	0.997	0.0005	1.06	0.999
Er—Lu	0.0011	1.78	0.995	−0.0007	0.76	0.988
DPTA						
La—Nd	0.0004	1.37	0.999	0.0007	0.76	0.867
Gd—Ho	0.0019	1.65	0.995	0.0006	1.10	0.999
Er—Lu	0.0000	1.82	1.000	−0.0012	0.75	0.967
α,β,β'-trihydroxyisobutyrate						
La—Nd	0.0062	3.16	0.988	0.0034	1.81	0.890
Gd—Ho	0.0005	−0.017	−0.03	0.0012	−0.012	−0.03
Er—Lu	−0.0003	2.13	0.998	−0.0013	0.87	0.954
thioglycolate						
La—Nd	−0.0058	0.88	0.917	−0.0012	0.39	0.639
Gd—Ho	−0.0043	−1.23	−0.969	−0.0034	−0.805	−0.981
Er—Lu	0.0000	1.34	0.969	0.0000	0.529	0.893
methoxyacetate						
La—Nd	−0.0006	0.82	0.963	−0.0008	0.48	0.871
Gd—Ho	−0.0039	0.11	0.394	−0.0037	0.06	0.348
Er—Lu	−0.0014	0.31	0.796	−0.0008	0.10	0.616
propionate						
La—Nd	−0.0180	3.13	0.913	0.0015	1.69	0.915
Gd—Ho	−0.0126	−1.96	−0.886	−0.010	−1.31	−0.916
Er—Lu	−0.011	1.04	0.548	−0.0063	0.260	0.321

Table 1 (continued)

Tetrad	Ligand					
	Eq. (1)			Eq. (2)		
	a	*b*	p^2	*a*	*b*	p^2
			picolinate			
La—Nd	0.0034	2.13	0.988	0.0025	1.20	0.875
Gd—Ho	0.0034	1.32	0.980	0.0025	0.87	0.990
Er—Lu	0.0007	1.51	0.991	−0.0009	0.64	0.991
			cis-1,3-*DCTA*			
La—Nd	−0.0051	2.49	0.991	−0.0001	1.27	0.797
Gd—Ho	0.014	2.99	0.943	0.011	1.98	0.961
Er—Lu	0.0002	1.15	0.981	−0.0012	0.49	0.986
			cis-1,4-*DCTA*			
La—Nd	0.015	0.97	0.688	0.0002	0.85	0.956
Gd—Ho	0.0092	2.12	0.962	0.0078	1.39	0.969
Er—Lu	−0.0039	1.57	0.955	−0.0041	0.62	0.885
			trans-1,4-*DCTA*			
La—Nd	−0.0039	1.77	0.989	0.0004	0.89	0.782
Gd—Ho	−0.0003	1.98	1.0000	−0.0011	1.27	0.996
Er—Lu	0.0019	1.88	0.993	0.0000	0.79	0.984
			isobutyrate			
La—Nd	0.0033	3.73	0.993	0.0037	2.06	0.862
Gd—Ho	0.0026	−2.70	−0.994	0.0040	−1.75	−0.995
Er—Lu	−0.010	3.05	0.920	−0.010	1.19	0.838
			α-hydroxyisobutyrate			
La—Nd	0.0039	2.70	0.993	0.0024	1.52	0.873
Gd—Ho	0.110	2.33	0.952	0.0092	1.53	0.965
Er—Lu	0.0031	2.35	0.988	0.0007	0.9967	0.983
			acetate			
La—Nd	−0.0020	1.97	0.989	0.0017	1.01	0.780
Gd—Ho	−0.0072	−1.99	−0.973	−0.0059	−1.30	−0.980
Er—Lu	−0.0032	1.093	0.887	−0.0018	0.39	0.742
			NTA			
La—Nd	0.0028	1.69	0.994	0.0011	0.976	0.900
Gd—Ho	−0.0028	0.80	0.973	−0.0029	0.511	0.960
Er—Lu	0.0000	1.57	1.000	−0.0011	0.652	0.970

Tetrad	Ligand					
	Eq. (1)			Eq. (2)		
	a	*b*	p^2	*a*	*b*	p^2
1-(2-arsophenylazo)-2-hydroxy-3,6-naphtalenedisulfonate						
La—Nd	−0.0014	0.55	0.976	−0.0005	0.29	0.801
Gd—Ho	0.0033	1.33	0.987	0.0026	0.87	0.989
Er—Lu	−0.0006	1.24	0.986	−0.0007	0.49	0.916
8-hydroxy-5,7-diiodoquinoline (= $C_9H_5I_2NO$)						
La—Nd	−0.0020	1.97	0.995	−0.0007	1.07	0.845
Gd—Ho	−0.0002	1.06	1.000	−0.0006	0.686	0.995
Er—Lu	0.0025	1.55	0.938	−0.0005	0.700	0.993
1-(1-naphtylazo)-2-naphtol						
La—Nd	−0.0027	0.81	0.973	−0.0007	0.40	0.761
Gd—Ho	−0.0021	1.48	0.943	−0.0029	0.96	0.991
Er—Lu	−0.0012	0.91	0.943	−0.0007	0.34	0.833
1-(2-naphtylazo)-2-naphtol						
La—Nd	0.0010	0.76	0.985	0.0008	0.39	0.783
Gd—Ho	−0.0002	1.38	0.994	−0.0010	0.90	0.998
Er—Lu	−0.0014	1.10	0.968	−0.0011	0.42	0.872
2,4-dihydroxybenzaldehyde oxime						
La—Nd	−0.0029	2.08	0.996	0.0000	1.09	0.822
Gd—Ho	−0.0012	2.55	0.998	0.0000	1.40	1.000
Er—Lu	0.0061	1.50	0.65	−0.0007	0.80	0.808
hydroxyiminoacetone						
La—Nd	−0.0034	2.06	0.994	0.0004	1.06	0.806
Gd—Ho	0.0014	1.17	0.996	−0.0008	0.76	0.998
Er—Lu	0.0022	1.08	0.832	−0.0009	0.52	0.932
3-hydroxyimino-2,4-pentanedione						
La—Nd	−0.0029	1.56	0.993	0.0001	0.80	0.796
Gd—Ho	0.0044	3.07	0.995	0.0035	1.98	0.992
Er—Lu	0.0068	0.83	0.58	0.0021	0.47	0.769
2-hydroxyimino-1-phenylethanone						
La—Nd	−0.0012	0.76	0.994	0.0001	0.80	0.796
Gd—Ho	0.0004	0.90	0.986	0.0035	1.98	0.992
Er—Lu	0.0035	1.34	0.824	0.0021	0.47	0.769
2-hydroxyacetophenone oxime						
La—Nd	−0.0020	2.16	0.994	0.0014	1.12	0.815
Gd—Ho	−0.0008	1.23	0.999	−0.0014	0.79	0.994
Er—Lu	0.0038	1.88	0.836	−0.0014	0.90	0.935

Table 1 (continued)

Tetrad	Ligand					
	Eq. (1)			Eq. (2)		
	a	*b*	p^2	*a*	*b*	p^2
4-hydroxy-3-coumarinyl methyl ketone oxime						
La—Nd	−0.0037	1.68	0.989	0.0004	0.85	0.781
Gd—Ho	−0.0026	1.79	0.995	−0.0032	1.15	0.988
Er—Lu	0.0052	0.992	0.623	0.0002	0.54	0.793
3-hydroxyimino-2-oxo-2,3-dihydro-1*H*-indole-5-sulfonate						
La—Nd	−0.0016	1.04	0.995	0.0000	0.55	0.819
Gd—Ho	−0.0015	1.28	0.995	0.0002	1.15	0.988
Er—Lu	0.0017	1.11	0.945	0.0002	0.54	0.793

Table 2. *List of ligands*

Ligand	Ref.
EDTA-ethylenediamine-N,N,N′,N′-tetraacetate	[14]
PDTA-1,2-propylenediamine-N,N,N′,N′-tetraacetate	[14]
DBTA-1,2-diaminobutane-N,N,N′,N′-tetraacetate	[14]
DCTA-diaminocyclohexane-N,N,N′,N′-tetraacetate	[18]
DPTA-1,2-diaminopentane-N,N,N′,N′-tetraacetate	[14]
α,β,β'-trihydroxyisobutyrate	[15]
thioglycolate	[16]
methoxyacetate	[16]
propionate	[16]
picolinate	[17]
isobutyrate	[15]
α-hydroxyisobutyrate	[15]
acetate	[19]
1-(1-arsophenylazo)-2-hydroxy-3,6-naphtalenedisulfonate	[20]
8-hydroxy-5,7-diiodoquinoline	[20]
1-(1-naphtylazo)-2-naphtol	[20]
1-(2-naphtylazo)-2-naphtol	[20]
2,4-dihydroxybenzaldehyde	[20]
hydroxyiminoacetone	[20]
3-hydroxyimino-2,4-pentanedione	[20]
2-hydroxyimino-1-phenylethanone	[20]
2-hydroxyacetophenone oxime	[20]
4-hydroxy-3-coumarinyl methyl ketone	[20]
3-hydroxyimino-2-oxo-2,3-dihydro-1*H*-indole-5-sulfonate	[20]
NTA-nitrilotriacetic acid	[21]

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