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Correlation in the Lanthanide Series

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Summary. The correlations lg K vs. lg K', V vs. V' (K – stability constant of the complex, V – unit cell volume of compound) within the lanthanide tetrads were reviewed. Ligands with – C = N-group were found to show a positive deviation from the lg K vs. lg K' plot.

Keywords. Lanthanide tetrads; Stability constant; Unit cell volume; Covalency.

Korrelation in der Lanthanidenserie

Zusammenfassung. Es wurden die Korrelationen lg K gegen lg K' und V gegen V' (wobei K die Stabilitätskonstante des Komplexes ist und V das Einheitszellenvolumen) innerhalb der Lanthanidentetraden untersucht. Bei Liganden mit – C = N-Gruppen wurde eine positive Abweichung von der lg K – lg K'-Geraden festgestellt.

Introduction

It was established in the previous paper [1] that there is a relationship between lg K (first stability constant of complex) and $1/r$ or $\sum_{1}^{3} I$ (ionization potential) within the lathanide tetrads. Now we want to find out whether there is a correlation lg K vs. lg K' (K and K' refer to the first stability constant of the same complex for the different lanthanides). It would be a new way in the expression of the microsymmetry which exists in the lanthanide series.

Results and Discussion

Figs. 1–3 represent the lg K vs. lg K' plot for three lanthanide tetrads. The tetrad Pm – Gd was omitted in respect to the lack of the data for Pm. The correlation for the first tetrad is unsatisfactory due to the strong deviation from the plot in the case of N-salicylidene-d-valine [$(OH)C_6H_4CH = NCH(COOH)CH(CH_3)_2$] and its derivatives. For the majority of complexes the coordination number in the La – Nd range is constant and the same is the case with the structure. There are other effects such as: ligand field, covalency in metal-ligand bond, ring formation which would be responsible for the above mentioned deviation. Almost all ligands

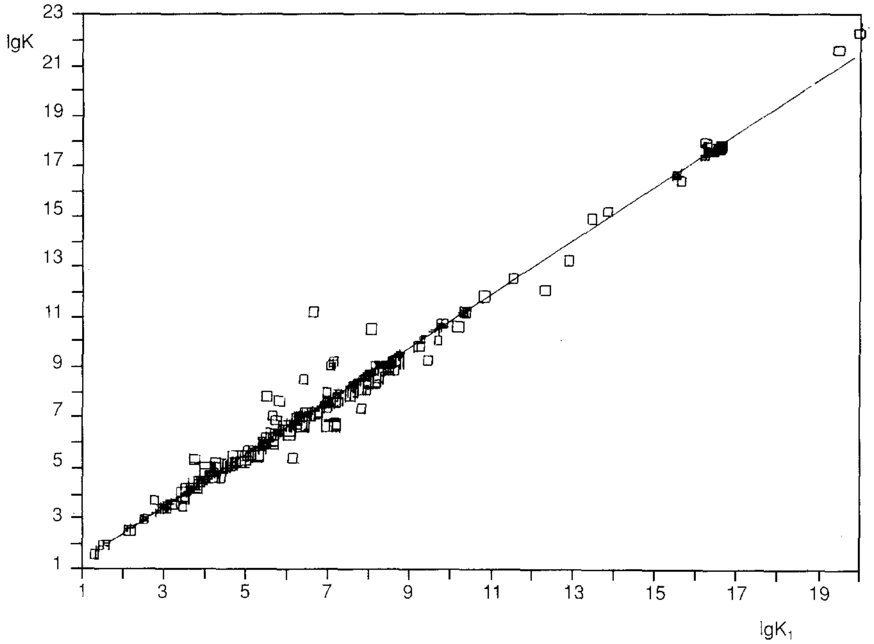


Fig. 1. Plot of the relationship $\lg K_{\mathrm{Nd}}$ vs. $\lg K_{\mathrm{La}}$ ($\lg K_{\mathrm{Nd}} = 1.0552 \cdot \lg K_{\mathrm{La}} + 0.2598$; $R^2 = 0.9787$)

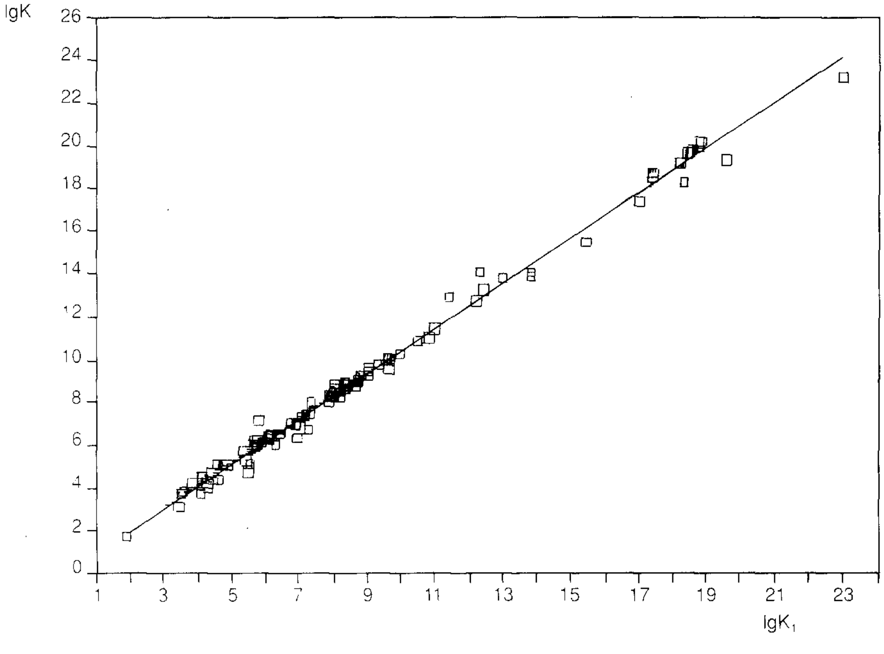


Fig. 2. Plot of the relationship $\lg K_{\mathrm{Ho}}$ vs. $\lg K_{\mathrm{Gd}}$ ($\lg K_{\mathrm{Ho}} = 1.0553 \cdot \lg K_{\mathrm{Gd}} - 0.1043$; $R^2 = 0.9936$)

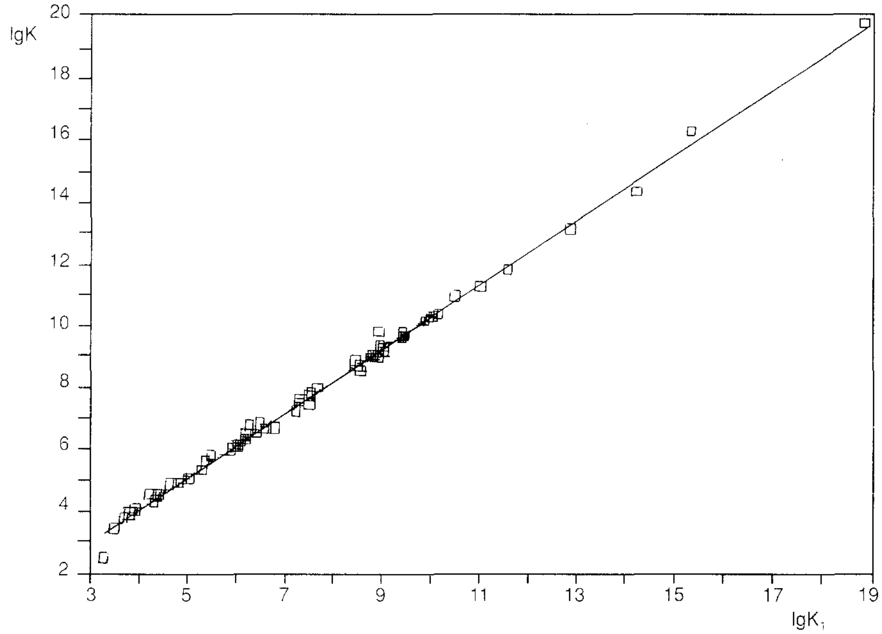


Fig. 3. Plot of the relationship $\lg K_{\mathrm{Lu}}$ vs. $\lg K_{\mathrm{Er}}$ ($\lg K_{\mathrm{Lu}} = 1.0479 \cdot \lg K_{\mathrm{Er}} - 0.1332$; $R^2 = 0.9965$)

which do not obey the $\lg K$ vs. $\lg K'$ rule possess mobile π electrons from a $-\mathrm{C}=\mathrm{N}-$ group, which are able to participate in formation of covalent metal-ligand bond (see Table 1). On the other hand it is known that the covalency in lanthanide complexes is very small [2–5] and it is very difficult to differentiate between covalency and ligand field effect; from this viewpoint the conclusion about the π electrons may be regarded as a presumption as well. The correlation in the Gd – Ho and Er – Lu tetrads is good but there are ligands which do not obey the rule. For example acetates, propionates, gluconates show a negative deviation in the Gd – Ho tetrad; diethylenetriamine-N,N,N′,N′-pentaacetates, bis(2-aminoethyl)ether-N,N,N′,N′-tetraacetates show negative deviations in the Er – Lu tetrad. This is not surprising because we know that such effects, as inner vs. outer sphere complexation or change of the coordination number of the central ion, usually occur in the middle of the lanthanide series. On the other hand in the case of bulky ligands like *EEDTA* steric hindrance in chelate formation would occur.

Trying to look for the analogy of the "correlation phenomenon" in the solid lanthanide compounds we may pay attention to the unit cell volumes dimensions, which similary to $\lg K$ values are the function of the ionic radius of the lanthanide. Figs. 4–6 show plots of V vs. V_1 for three different tetrads. In all three cases we have excellent correlation, above 99.9%. How to explain such a good fit, which is better than in the case of $\lg K$ vs. $\lg K'$ plots? It seems that solid lanthanide compounds obey better the "ionic radius rule" than the complexes of the lanthanides in the solution. The "rigidity" of ions in the solid state and therefore their looseness in contact with counterions minimizes the ligand field effect. Although all this considerations may be considered speculative, one thing is evident from the practical

Table 1. List of ligands reviewed with respect to the rule: lg K vs. lg K_1 (ligands which do not obey the rule are marked by asterisks*)

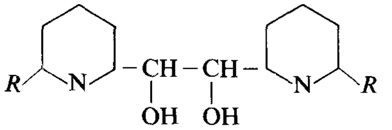
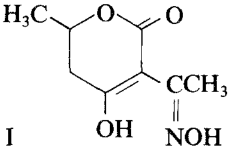
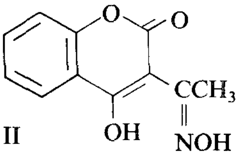
No.	Ligand	Ref.
1.	2-Aminophenol	[6]
2.	 R=H (ligand I = $C_{12}H_{12}N_2O_2$) R=CH_3 (ligand II = $C_{14}H_{16}N_2O_2$)	[6]
3.	8-Hydroxyquinoline	[6]
4.	8-Hydroxy-5,7-dinitroquinoline	[6]
5.	5,7-Dichloro-8-hydroxyquinoline	[6]
6.	5,7-Dibromo-8-hydroxyquinoline	[6]
7.	8-Hydroxy-5,7-diiodoquinoline	[6]
8.	8-Hydroxy-5-quinolinesulfonic acid	[6]
9.	8-Hydroxy-7-nitro-5-quinolinesulfonic acid	[6]
10.	7-Bromo-8-hydroxy-5-quinolinesulfonic acid	[6]
11.	8-Hydroxy-7-iodo-5-quinolinesulfonic acid	[6]
12.	8-Hydroxy-2-methylquinoline	[6]
13.	5,7-Dichloro-8-hydroxy-2-methylquinoline	[6]
14.*	2-(Salicylideneamino)ethanesulfonic acid	[6]
15.*	N-Salicylidene-valine (2-OH) $C_6H_4CH=NCH(COOH)CH(CH_3)_2$	[6]
16.	2-(Salicylideneamino)phenol	[6]
17.	3-(Salicylideneamino)phenol	[6]
18.	4-(Salicylideneamino)phenol	[6]
19.	N-Salicylidene-*o*-anisidine	[6]
20.	N-Salicylidene-*m*-anisidine	[6]
21.	N-Salicylidene-*p*-anisidine	[6]
22.	N-Salicylidene-*p*-thioanisidine	[6]
23.*	4-(Salicylideneamino)phenyl-thioacetic acid	[6]
24.	2-[1-(2-Hydroxyphenyl)ethylideneamino]benzenesulfonic acid	[6]
25.*	N-[1-(2-Hydroxyphenyl)ethylidene]valine	[6]
26.	2-[(1-Methyl-3-oxobutylidene)amino]ethanesulfonic acid	[6]
27.*	N-(1-Methyl-3-oxobutylidene)-anthranilic acid	[6]
28.*	N-(1-Methyl-3-oxo-3-phenyl-1-propylidene)anthranilic acid	[6]
29.*	2-[3-Oxo-1-phenylbutylidene)amino]benzenesulfonic acid	[6]
30.	3-Formyl-4-hydroxyazobenzene	[6]
31.	1-Phenylazo-2-naphtol	[6]
32.	1-(1′-Naphtylazo)-2-naphtol	[6]
33.	1-(2′-Naphtylazo)-2-naphtol	[6]
34.	4-(2-Pyridylazo)-1,3-benzenediol	[6]
35.	1-(2-Pyridylazo)-2-naphtol	[6]
36.	Chlorophosphonazo III	[6]
37.	Thoron	[6]
38.	Arsenazo I	[6]
39.	2,4-Dihydroxybenzaldehyde oxime	[6]
40.	2-Pyridinecarbaldehyde oxime	[6]
41.	6-Methyl-2-pyridinecarbaldehyde oxime	[6]
42.	Hydroxyiminoacetone	[6]
43.	2-Hydroxyacetophenone oxime	[6]

Table 1 (continued)

No.	Ligand	Ref.
44.	Monoximes derived from dehydroacetic acid and 3-Acetyl-4-hydroxycoumarin I  II 	[6]
45.	1-Nitroso-2-naphtol	[6]
46.	2-Nitroso-1-naphtol	[6]
47.	Biacetyl dioxime	[6]
48.	Dioxime derived from dioxo- and trioxo-compounds: I = Methylglyoxal dioxime, II = 2,3,4-Pentanentrione 2,3-dioxime, III = Phenylglyoxal dioxime	[6]
49.	2-Pyridinecarboxylic acid N-oxide	[6]
50.	1-Hydroxy-2-oxo-1,2-dihydroquinoline	[6]
51.	8-Hydroxyquinoline N-oxide	[6]
52.	8-Hydroxy-2-methylquinoline N-oxide	[6]
53.	1,5-Diphenylcarbazone	[6]
54.	N-Phenyl-3-oxobutyrohydroxamic acid	[6]
55.	Benzohydroxamic acid	[6]
56.	3-Nitrobenzohydroxamic acid	[6]
57.	2-Hydrobenzohydroxamic acid	[6]
58.	Purpuric acid	[6]
59.	Ethylenediamine-N,N,N′,N′-tetraacetatic acid	[7]
60.	*trans*-1,2-Diaminocyclohexane-N,N,N′,N′-tetraacetic acid	[7]
61.	N′-Hydroxyethylenediamine-N,N,N′-triacetic acid	[7]
62.*	Diethylenetriamine-N,N,N′,N′-pentaacetic acid	[7]
63.*	Bis(2-aminoethyl)ether-N,N,N′,N′-tetraacetic acid	[7]
64.	Ethyleneglycolbis(2-aminoethyl)ether-N,N,N′,N′-tetraacetic acid	[7]
65.	Ethylenediamine-N,N′-dimalonic acid	[7]
66.	Ethylenediamine-N,N′-disuccinic acid	[7]
67.	1,2-Diaminopentane-N,N,N′,N′-tetraacetic acid	[7]
68.	1,2-Diaminohexane-N,N,N′,N′-tetraacetic acid	
69.	Ethylenediamine-N,N′-diacetic acid	[7]
70.	Iminodiacetic acid	[8]
71.	N-Methyliminodiacetic acid	[8]
72.	N-Benzyliminodiacetic acid	[8]
73.	N-Phenyliminodiacetic acid	[8]
74.	N-Hydroxyethyliminodiacetic acid	[8]
75.	N-Methoxyethyliminodiacetic acid	[8]
76.	N-Methylmercaptoethyliminodiacetic acid	[8]
77.	N-(2-Picolyl)iminodiacetic acid	[8]
78.	N-(6-Methyl-2-picolyl)iminodiacetic acid	[8]
79.	Acetylacetone	[14]
80.	Isobutyric acid	[14]
81.	Trihydroxyisobutyric acid	[14]
82.*	Acetic acid	[14]
83.*	Propionic acid	[14]
84.*	Gluconic acid	[14]
85.*	Glycolic acid	[14]

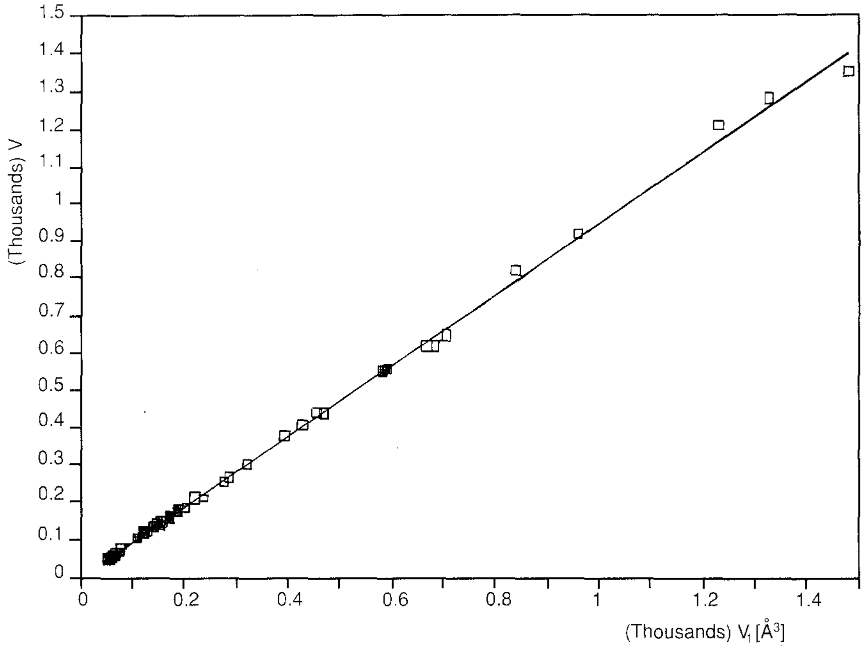


Fig. 4. Plot of the relationship V_{Nd} vs. V_{La} ($V_{Nd} = 0.9499 \cdot V_{La} - 0.1287$; $R^2 = 0.9985$); the following ligands were reviewed: LnAlO$_3$ [7], LnScO$_3$ [7], LnVO$_3$ [7], LnCrO$_3$ [7], LnMnO$_3$ [7], LnFeO$_3$ [7], LnGaO$_3$ [7], LnRhO$_3$ [7], LnInO$_3$ [7], LnHg [9], LnHg$_2$ [9], LnHg$_3$ [9], LnHg$_4$ [9], LnNi$_2$ [9], LnNi$_5$ [9], LnN [9], LnO [9], Ln_2O$_3$ [9], LnP [9], LnPt$_2$ [9], LnRh$_2$ [9], LnSe [9], Ln_2Se$_4$ [9], LnSi$_2$ [9], LnAg [9], LnS [9], Ln_3S$_4$ [9], LnTe [9], LnTl [9], LnTl$_3$ [9], LnSn$_3$ [9], LnCd$_2$ [9], LnB$_6$ [9], LnB$_4$ [9], LnBi [9], LnAs [9], LnSb [9], LnAl$_2$ [9], LnAl$_4$ [9], Ln_2C$_3$ [9], LnC$_2$ [9], Rb$_2$$LnCl_5$ [10], Cs$_2$KLnF$_6$ [10], Cs$_2$KLnCl$_6$ [10], Cs$_2$LiLnBr$_6$ [10], Cs$_2$NaLnBr$_4$ [10], NaLnF$_4$ [10], Ln(H$_2$O)$_9$(C$_2$H$_5$SO$_4$)$_3$ [11], Ln(H$_2$O)$_9$(BrO$_3$)$_3$ [11], trisodium-tris(oxydiacetato)-lanthanide III [12], Ln[SiO$_4$]O [13], LiLn_9[SiO$_4$]$_6$O$_2$ [13], NaLn_9(SiO$_4$)$_6$O$_2$ [13]

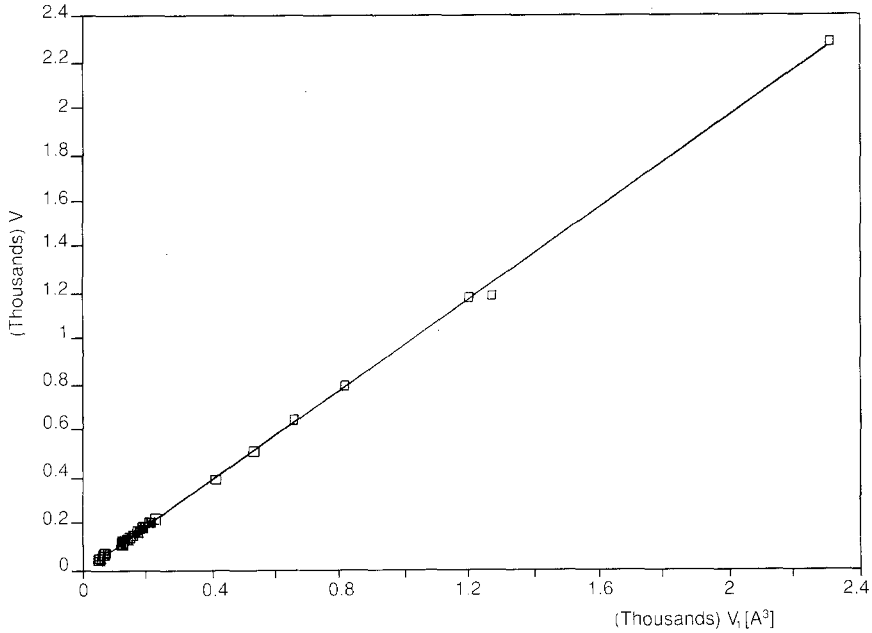


Fig. 5. Plot of the relationship V_{Ho} vs. V_{Gd} ($V_{Ho} = 0.9836 \cdot V_{Gd} - 3.314$; $R^2 = 0.9995$)

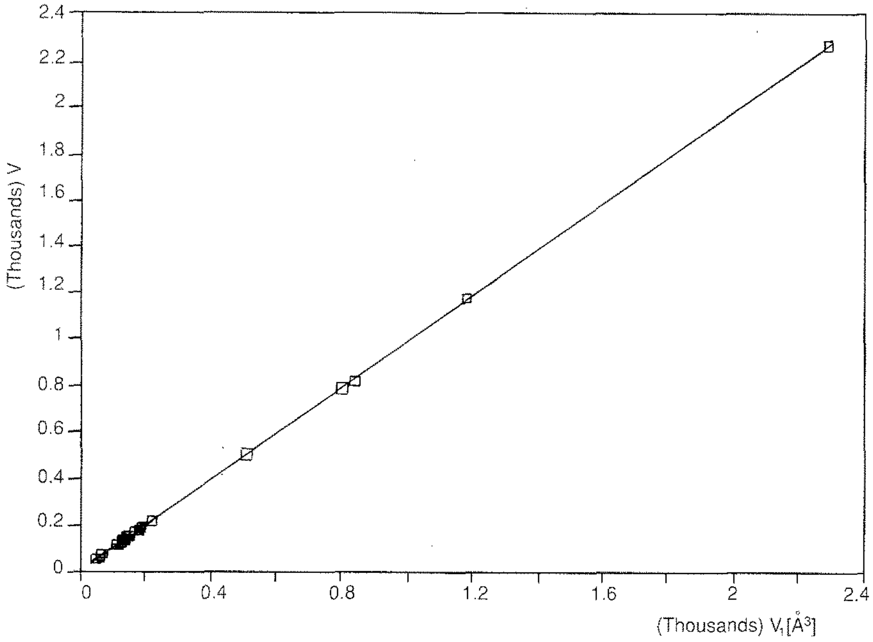


Fig. 6. Plot of the relationship V_{Lu} vs. V_{Er} ($V_{\mathrm{Lu}} = 0.9934 \cdot V_{\mathrm{Er}} - 2.6946$; $R^2 = 0.9999$)

point of view: the good correlation in lg V vs. lg V_1 may be used in the prediction of unknown values of the dimensions of the unitcell volumes.

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