Monatshefte für Chemie 124, 681–687 (1993)

Monatshefte für Chemie
Chemical Monthly

Yttrium(III) Bonding to Organic Ligands: A Comparison with the Lanthanoid(III) Cations

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Summary. The yttrium(III) bonding to organic substrates (oximes, β-diketonates and (poly)amino-(poly)carboxylates) has been compared with that of the lanthanoid(III) cations. The complexation constants of Y^{3+} with the examined organic ligands are similar to those of some cations of the first half of the lanthanoid series, in contrast with the fact that the Y^{3+} ionic dimensions are similar to those of Ho^{3+}. This has been explained by correlating the formation constants of the Y^{3+} and the lanthanoids(III) complexes by the equation $\log K_1 = C_A C_B + E_A E_B$, where the parameters C and E indicate the tendency of each Lewis acid A and Lewis base B to undergo covalent or ionic bonding, and where the ratio $H = E/C$ indicates the charge control on the bond formation tendency of each species A or B. The results are commented in terms of the utility of Y^{3+} in assisting organic reactions.

Keywords. Yttrium; Lanthanoids; Rare earths; Complexation constants; Statistics.

Bindung von Yttrium(III) an organische Liganden: Vergleich mit Lanthanoid(III)-Kationen

Zusammenfassung. Es wurde die Bindung von Yttrium(III) an organische Substanzen [Oxime, β-Diketonate und (Poly)Amino(poly)carboxylate] im Vergleich mit Lanthanoid(III)-Kationen behandelt. Die Komplexierungskonstanten von Y^{3+} sind ähnlich denen einiger Kationen der ersten Hälfte der Lanthanoidenserie; dies steht im Gegensatz zur Tatsache, daß die Dimensionen des Y^{3+}-Ions denen des Ho^{3+} entsprechen. Die Erklärung wurde mittels der für die Bildungskonstanten der Y^{3+}- und Lanthanoid(III)-Komplexe gültigen Gleichung $\log K_1 = C_A C_B + E_A E_B$ gefunden, wobei C und E Parameter sind, die die Tendenz der Lewis-Säuren A und der Lewis-Basen B zum Eingehen von kovalenten oder ionischen Bindungen charakterisieren und wo das Verhältnis $H = E/C$ den Steuerungseffekt der Ladung auf die Bindungstendenz der Spezies A oder B beschreibt. Die Ergebnisse werden im Hinblick auf den Nutzen von Y^{3+} zur Unterstützung organischer Reaktionen diskutiert.

Introduction

The use of rare earth cations as reagents or catalysts in organic reactions has recently been reviewed [1–6]. A relevant branch in this field consists in the exploitation of the Lewis acid features of the lanthanoid(III) cations, allowing a number of reactions to occur under mild conditions.

The various Ln^{3+} ions often present significant differences in their effectiveness in promoting organic reactions. For example, it has been reported that the late lanthanoid salts ($DyCl_3$, $TmCl_3$, and $LuCl_3$) have particularly high activity in catalyzing Friedel-Crafts alkylation processes, whereas $LaCl_3$ possesses little catalytic activity [7]; Yb(*fod*)$_3$ is more effective catalyst than Eu(*fod*)$_3$ in some Diels–Alder and hetero-Diels–Alder reactions [8]; light lanthanoid salts ($LaCl_3$, $CeCl_3$ and $NdCl_3$) effect rapidly and with high yields the acetalization of aliphatic linear aldehydes, while heavier salts ($ErCl_3$ and $YbCl_3$) are superior for aromatic and cyclic aldehydes [9].

In order to better understand the reasons for these differences in reactivity, we focused our attention on some simple organic reactions promoted by Ln^{3+} cations and described the importance of the Ln^{3+} size, the counterion and the solvent [10–12]. Moreover, the charge and frontier orbital control on the bonding between Ln^{3+} cations and organic substrates has been examined in detail, observing that going from La^{3+} to Lu^{3+} the ionic contribution of the metal-ligand bond increases less than the covalent one [13].

At present, we are extending our interests to a wider classes of substrates and to the lightest rare earth cations, Sc^{3+} and Y^{3+}; in particular, we found that rare earth cations catalyze the Meerwein–Ponndorf–Verley reduction of aldehydes and ketones; in the case of the reduction of *p*-nitrobenzaldehyde to *p*-nitrobenzilic alcohol, the pseudo-first order kinetic constant of the Y^{3+} catalyzed process ($3.0 \times 10^{-5}\,s^{-1}$) is intermediate between those of the La^{3+} catalyzed ($0.3 \times 10^{-5}\,s^{-1}$) and of the Lu^{3+} catalyzed ($3.6 \times 10^{-5}\,s^{-1}$) processes [14]. This could be explained by the fact that the reduction process is Lewis acid promoted and that the Lewis acidity is proportional to the charge density of the cation. Therefore, the ion Y^{3+} +, whose ionic radius is close to that of Ho^{3+} [15], would behave like Ho^{3+}, i.e. would possess a catalytic activity intermediate between those of La^{3+} and Lu^{3+}. However, it is also possible that the catalytic behaviour of Y^{3+} is different from that of the lanthanoid(III) cations because of a qualitative difference between their bonding to organic molecules. In the present paper, we compare the Y^{3+} bonding to organic substrates with that of the lanthanoid(III) cations, in order to point out eventual differences between the two situations.

Method

The relative stability of the Y^{3+} complexes versus the Ln^{3+} ones has been evaluated with the ratio

$$\log K_{i,Ln}/\log K_{i,\mathrm{Y}} \tag{1}$$

where $i = 1$ or 2, and $K_{i,Ln}$ and $K_{i,\mathrm{Y}}$ are the complexation constants of Ln^{3+} and Y^{3+} with a given ligand. We considered the complexation constants with three classes of ligands which have been widely studied: ligands containing an oximic function (referred to as "oximes"), β-diketonates ("carbonyls") and (poly)amino(poly)carboxylates ("carboxylates"). The three classes of ligands were considered separately in order to avoid as far as possible any misjudgment due to their different electronic properties and their different ways of interaction with the metals. Data determined under different experimental conditions were considered together, since it seems unlike that the ratios (1) are affected by the absolute values of the complexation constants. Table 1 reports for all Ln^{3+} ions the mean value of the above defined ratios, $\langle \log K_{i,Ln}/\log K_{i,\mathrm{Y}} \rangle$, the number of cases examined, and the t test value defined as

$$t = |1 - \langle \log K_{i,Ln}/\log K_{i,\mathrm{Y}} \rangle| / \sigma(\langle \log K_{i,Ln}/\log K_{i,\mathrm{Y}} \rangle) \tag{2}$$

where $\sigma(\langle \log K_{i,Ln}/\log K_{i,\mathrm{Y}} \rangle)$ is the standard deviation of the mean; the meaning of the t parameter is the following: if $t \leqslant 1.960$, the Ln^{3+} behaviour is statistically equivalent to that of Y^{3+} [19].

The covalent and electrostatic contribution to the metal-ligand bonds were evaluated by applying the following numerical approach to the frontier orbital concept:

$$\log K_1 = C_A C_B + E_A E_B \tag{3}$$

where, as described by Drago [20, 21] and Hancock [22–24], C_A and C_B are a measure for the strength of the covalent contribution to the metal-ligand bond for the acid A and the base B, and E_A and E_B correspond to the ionic contribution of the metal-ligand bond. Although the absolute values of the parameters C_i and E_i $(i = A, B)$ depend on some fixed reference values, their ratio $H_i = E_i/C_i$ is independent of any fixed reference value and is taken as a measure of the relative ionicity versus covalence in the metal-ligand bond.

Equation (3) was applied separately to 22 "carboxylates" and 8 "oximes". No corrections were introduced but the complexation constant values were considered as they were published, since they were determined in identical experimental conditions. The fitting procedure of Eq. (3) has already been described. As a starting hypothesis, the C_A and E_A values recently determined by us for the Ln^{3+} ions were employed [13] together with the C_A and E_A values for Y^{3+} reported in Ref. [22]. Table 2 reports the C_A, E_A and H_A parameters for the cations, together with the average values of the differences ($\Delta \log K_1$) between calculated and experimental $\log K_1$ for each Ln^{3+} ion; the $\Delta \log K_1$ values indicate a satisfactory fit of Eq. (3) [13].

Results and Discussion

Figure 1 reports the dependence of the ratio $\log K_{1,Ln}/\log K_{1,Y}$ for the three classes of ligands on the atomic number. The well known subperiodicity within the lanthanoid series appears [25]: the ratio values increase going from La^{3+} to Lu^{3+}, with a break at the Gd^{3+} level. Some minor irregularities are present in the case of ligands "oximes" and "carbonyls", which cannot be explained in terms of the tetrad effect [25, 26]. Probably they are due to a statistical bias owing to the low number of observations. Moreover, as expected [27], in all the three cases it appears that the ratio values are much more variable within the first half (La–Gd) than within the second half (Gd–Lu) of the lanthanoid series.

Figure 1 gives a sound evidence of the fact that the Ln^{3+} ions which are more strictly similar to Y^{3+} are within the first half of the lanthanoid series. Quantitatively, it can be seen from Table 1 that the cations with a t value lower than 1.960 are Ce^{3+}, Pr^{3+} and Nd^{3+} in the case of ligands "oximes", Sm^{3+} and Eu^{3+} in the case of ligands "carbonyls", and Sm^{3+}, Eu^{3+} and Gd^{3+} in the case of ligands "carboxylates". Similar trends are found by considering the second complexation constants, although they are less variable especially within the second half of the lanthanoid series (the differences between $\log K_{2,\mathrm{Lu}}/\log K_{2,\mathrm{Y}}$ and $\log K_{2,\mathrm{Gd}}/\log K_{2,\mathrm{Y}}$ are only 0.037, 0.019, and 0.013, while in the case of the first complexation constants they are 0.050, 0.057, and 0.079 for the three classes of ligands), and therefore more cations behave statistically as Y^{3+}.

The result that Y^{3+} has an average affinity for the examined organic ligands similar to some cations of the first half of the lanthanoid series is markedly in contrast with the ionic dimensions arising from the analysis of the solid state structures. In fact the Y^{3+} ionic radius following Shannon [15] is close to that of Ho^{3+}: for the coordination number ranging from 6 to 8 and to 9, the ionic radii of Y^{3+} and Ho^{3+} are 0.900, 1.019, and 1.075 Å and 0.901, 1.015, and 1.072 Å, respectively. Also the more recent atomic dimensions calculated by O'Keeffe [28] indicate that Y^{3+} is much more similar to the heavier lanthanoid(III) cations than

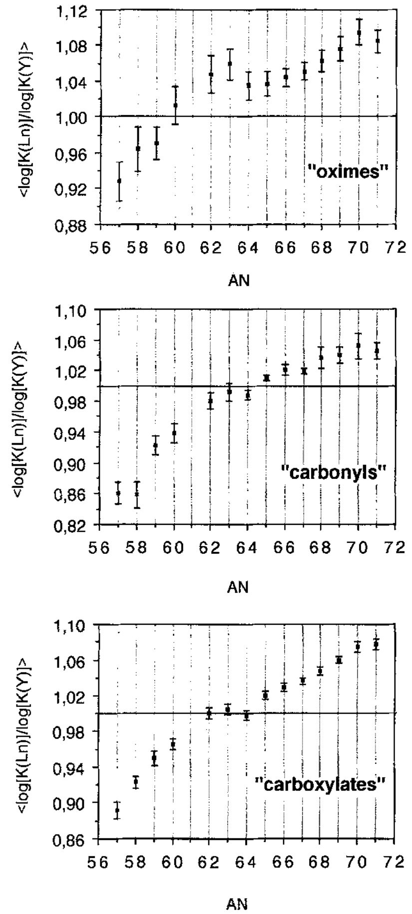

Fig. 1. Dependence of the mean values of the ratios $\log K_{1,Ln}/\log K_{1,\mathrm{Y}}$ [see Eq. (1)] on the atomic number for the three classes of ligands

to the lighter ones. It is therefore reasonable to suppose that the Y^{3+} complexation constants differ from those of the heavier Ln^{3+} ions because of the nature of the binding to organic ligands.

One of the simplest ways to evaluate the type of bonding between Lewis acids and bases is based on the concept of charge and frontier orbital control. An approach to the frontier orbital concept is given by Eq. (3), which has already been applied to study the relative covalent and electrostatic contributions to the bonds involving lanthanoid(III) cations [13]. By fitting Eq. (3) with the complexation constant data concerning the "oxime" and the "carboxylate" complexes of Ln^{3+} and Y^{3+}, we obtained the results shown in Table 2. Concerning the Ln^{3+} ions they are very similar, independently of the class of ligands examined, and they closely resemble the C_A, E_A, and H_A parameters already calculated, which were discussed in terms of LUMO energy of the Ln^{3+} ions, and which indicate that the covalent character of the Ln^{3+}-ligand bond increases with the atomic number [13]. Concerning the Y^{3+} ion it appears that both its covalent (C_A) and electrostatic (E_A) contribution to the metal-ligand bond are similar to those of the light Ln^{3+} ions. However, the $H_A = E_A/C_A$ ratio of Y^{3+}, which is nearly an "absolute" quantity indicating the hardness of the cation [13, 22–24], is lower than those of all the Ln^{3+} ions with the

Table 1. Mean values of the ratio defined in Eq. (1) with the estimated standard deviations ($\times 10^3$) in parentheses, number of observations and t parameter values defined in Eq. (2)

Oximes						
Ln	$\langle \log K_{1,Ln}/\log K_{1,\mathrm{Y}} \rangle$	no. of cases	t	$\langle \log K_{2,Ln}/\log K_{2,\mathrm{Y}} \rangle$	no. of cases	t
La	0.928 (22)	18	3.273	0.902 (23)	10	4.261
Ce	0.964 (25)	18	1.440	0.910 (17)	9	5.294
Pr	0.970 (18)	18	1.667	0.938 (19)	10	3.263
Nd	1.013 (21)	20	0.619	0.964 (25)	10	1.440
Sm	1.048 (21)	19	2.286	1.030 (37)	10	0.881
Eu	1.059 (17)	15	3.471	1.015 (30)	10	0.500
Gd	1.035 (16)	20	2.188	1.005 (22)	10	0.227
Tb	1.037 (13)	14	2.846	1.038 (25)	9	1.520
Dy	1.044 (10)	20	4.400	1.061 (21)	11	2.905
Ho	1.051 (10)	19	5.100	1.078 (20)	10	3.900
Er	1.062 (12)	19	5.167	1.065 (26)	10	2.500
Tm	1.076 (14)	18	5.429	1.075 (19)	10	3.947
Yb	1.095 (15)	18	6.333	1.052 (19)	10	2.737
Lu	1.085 (13)	17	6.538	1.042 (25)	10	1.680
Carbonyls						
La	0.860 (14)	16	10.000	0.835 (18)	15	9.167
Ce	0.858 (17)	3	8.353	0.755 (102)	2	2.402
Pr	0.922 (12)	16	6.500	0.932 (17)	15	4.000
Nd	0.938 (13)	15	4.769	0.962 (17)	12	2.235
Sm	0.980 (11)	13	1.818	1.008 (20)	12	0.400
Eu	0.922 (11)	12	0.727	0.994 (18)	11	0.333
Gd	0.988 (6)	11	2.000	0.995 (19)	10	0.263
Tb	1.010 (4)	7	2.500	0.997 (14)	6	0.214
Dy	1.021 (7)	11	3.000	1.018 (15)	10	1.200
Ho	1.019 (3)	7	6.333	1.004 (13)	6	0.308
Er	1.037 (14)	11	2.643	1.028 (19)	10	1.474
Tm	1.040 (10)	6	4.000	1.017 (16)	5	1.062
Yb	1.052 (17)	9	3.059	1.048 (24)	9	2.000
Lu	1.045 (11)	5	4.091	1.014 (20)	4	0.700
Carboxylates						
La	0.892 (9)	73	12.000	0.836 (16)	37	10.250
Ce	0.923 (7)	65	11.000	0.872 (17)	30	7.529
Pr	0.950 (8)	64	6.250	0.941 (17)	37	3.471
Nd	0.966 (6)	63	5.667	0.954 (14)	37	3.286
Sm	1.001 (6)	63	0.167	1.001 (14)	34	0.071
Eu	1.005 (6)	57	0.833	1.016 (15)	32	1.067
Gd	0.998 (5)	65	0.400	1.017 (17)	34	1.000
Tb	1.020 (4)	53	5.000	1.042 (12)	34	3.500
Dy	1.029 (5)	64	5.800	1.058 (10)	33	5.800
Ho	1.036 (4)	51	9.000	1.061 (12)	33	5.083
Er	1.047 (4)	57	11.750	1.063 (10)	34	6.300
Tm	1.060 (4)	52	15.000	1.058 (16)	32	3.625
Yb	1.075 (6)	65	12.500	1.044 (15)	31	2.933
Lu	1.077 (6)	52	12.833	1.030 (21)	30	1.429

Table 2. Covalent (C_A), electrostatic (E_A) and charge control (H_A) parameters [see Eq. (3)] and average of the absolute values of the differences between the experimental and calculated $\log K_1$ ($\Delta \log K_1$)

Ln	*Oximes*				*Carboxylates*			
	C_A	E_A	H_A	$\Delta \log K_1$	C_A	E_A	H_A	$\Delta \log K_1$
Y	0.402	4.030	10.025	0.18	0.419	4.211	10.049	0.14
La	0.362	3.718	10.271	0.12	0.361	3.709	10.273	0.19
Ce	0.385	3.950	10.259	0.12	0.391	4.005	10.243	0.13
Pr	0.398	4.067	10.219	0.17	0.393	4.013	10.212	0.19
Nd	0.401	4.113	10.256	0.12	0.407	4.168	10.241	0.08
Sm	0.412	4.214	10.229	0.07	0.419	4.287	10.232	0.12
Eu	0.412	4.222	10.248	0.15	0.409	4.179	10.218	0.13
Gd	0.409	4.181	10.222	0.05	0.412	4.211	10.222	0.14
Tb	0.414	4.216	10.184	0.05	0.421	4.290	10.191	0.18
Dy	0.424	4.308	10.160	0.05	0.427	4.334	10.149	0.10
Ho	0.425	4.313	10.148	0.09	0.435	4.417	10.153	0.11
Er	0.437	4.422	10.119	0.11	0.441	4.455	10.101	0.19
Tm	0.442	4.448	10.063	0.08	0.443	4.452	10.050	0.04
Yb	0.450	4.514	10.031	0.09	0.453	4.562	10.071	0.09
Lu	0.452	4.529	10.020	0.15	0.458	4.585	10.012	0.15

exception of Lu^{3+}. By comparing the C_A and E_A parameters of the Y^{3+} and Ho^{3+} ions, which have the same charge and dimensions, it appears that both the covalent and the electrostatic contributions to the metal-ligand bond decrease in going from Ho^{3+} to Y^{3+}, but the electrostatic parameter decreases more than the covalent one. Consequently, the Y^{3+}-ligand bond assumes a higher covalent character than the Ho^{3+}-ligand one.

In order to rationalize the above results, it is necessary to assume that the electrostatic character of the metal-ligand bond is essential in stabilizing (thermodynamically) the complexes. Therefore, the Y^{3+} complexes stability is smaller than that of the heavier lanthanoid(III) cations, which have (namely Ho^{3+}) charge density closer to that of Y^{3+}, because the electrostatic contribution to the Y^{3+}-ligand bond is less important than that to the heavier Ln^{3+}-ligand bonds. The reason why the covalence of the Y^{3+}-ligand bonds is higher than that of the heavier Ln^{3+}-ligand bonds could be due to the availability of the 4d orbitals in the case of Y^{3+}: they are lower in energy than the 5d ones, which are available for covalent bonding in the case of the Ln^{3+} ions, and they are thus more easily involved in covalent bonding.

Such a trend can suggest that the use of Y^{3+} compounds in catalyzing organic reactions is promising, especially when a polarization is essential in activating an organic function, for instance when the organic substrate is a neutral molecule such as an aldehyde or a ketone. Our recent results support this hypothesis [14] and work is in progress to investigate also the behaviour of Sc^{3+}, which could show more extreme (but qualitatively analogous) behaviour than Y^{3+}.

Acknowledgements

This investigation was supported by MURST and CNR (Rome, Italy).

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Received June 30, 1992. Accepted September 18, 1992