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Structural investigations of N,N'-substituted malonamide crystal compounds as a basis to support trivalent lanthanide extraction mechanisms

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Abstract

The problem of bond energies in the nitrato compounds of trivalent lanthanides, Ln, with malonamides, L, of the type: $Ln(NO_3)_3(H_2O)_mL$ and $Ln(NO_3)_3L_2$, ($L=CH_2(OCNR_1R_2)_2$) is approached through a semi-empirical theory connecting thermodynamic with structural properties (STT). Emphasis is given on the relation between bond energies and solvent extraction of complexes of Ln with L from nitric aqueous solutions. STT is presented and applied to nitrato compounds with R_1=ethyl, R_2=ethyl, R_1=methyl, R_2=cyclohexyl and R_1=methyl, R_2=phenyl. For the first time, the effect of the regular decrease of the bond energies Ln–O(nitrato) and Ln–O(L) with the increase of the volume of L is evidenced. The enthalpies of extraction of Ln by L from low nitric acid concentration are calculated. Finally, rules connecting the distribution coefficients D(Ln) in liquid–liquid extraction of Ln (III) by diamides is formulated. These rules appear as a useful guide to predict D(Ln) variation along the series.

Keywords: Lanthanide; Diamide; Bond energy; Thermodynamic data; Solvent extraction

1. Introduction

Malonamides of the type $R_3CH(OCNR_1R_2)_2$, with R_1, R_2 and R_3 alkyl, oxyalkyl or phenyl groups, have been suggested as possible coextractants of the trivalent actinides, An, and lanthanides, Ln, from the high radioactive aqueous waste stream of the PUREX process [1]. At the present time, the extraction of Ln and An by L is analysed for low nitric acid concentration of the aqueous phase (up to 1 mol dm^{-3}) in the frame of a coordinative mechanism:

$$M^{3+}(aq) + 3NO_3^-(aq) + nL(org) = M(NO_3)_3L_n(org) \qquad (1)$$

where $n=1$ and 2. At higher concentrations of nitric acid, between 1 and 6 mol dm^{-3}, Ln and An seem to be extracted as ionic pairs, but as this paper deals with the coordinative extraction mechanism, the corresponding processes of the latter case are not considered [2–6].

In the following, the bond energies of Ln–O(nitrato), Ln–O(water) and Ln–O(L) in the compounds $Ln(NO_3)_3(H_2O)_mL$ and $Ln(NO_3)_3L_2$ for Ln=La, Nd, Er and Yb and $L=[(C_2H_5)_2NCO]_2CH_2$, $(CH_3C_6H_{11}CON)_2CH_2$ and $(CH_3C_6H_5NCO)_2CH_2$, which are tetraethyl malonamide, N,N'-dimethyl, N,N'-dicyclohexyl malonamide, and N,N'-dimethyl, N,N'-diphenyl malonamide, respectively, are calculated in the frame of the new structural thermodynamic theory (STT). The trend in the bond energy Ln–O across the series is discussed. From these data, estimation of the enthalpy of extraction of Ln with L is presented and discussed.

2. Results and discussion

2.1. Equations of STT

Let us write the total electronic energy E(tot) for the system with i atoms and j bonds through the pair interactions:

$$E(\text{tot}) = \Sigma_i E_{\text{at},i} + \Sigma_j D_{\text{o},j} \qquad (2)$$

where $E_{\text{at},i}$ is the total electron energy of an i-atom and

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$D_{o,j}$ is the interaction energy of the jth pair of atoms. Only interactions between Ln and the neighbouring elements are taken into account, that is to say the valent approximation is used. Exceptions will be mentioned. In the simple case of a diatomic system, A_2, the equations of STT [7] are written as follows:

$$D_o(AA) = k\theta_A^2 \tag{3}$$

$$\ln \theta_A = \chi_{SI}^{di}(A) + \gamma_A(AA) \tag{4}$$

where $k=1$ eV (1 eV/molecule = 96.485 kJ mol^{-1}). The function θ_A is determined through a structural independent parameter $\chi_{SI}^{di}(A)$ (di stands for diatomic and SI for specific interaction) and a structural dependent component $\gamma_A(AA)$, both dimensionless.

$$\gamma_A(AA) = (R_o^2(A) - R_e^2)(R_o(A)R_e)^{-1} \tag{5}$$

where:

(1) $R_o(A)$ is the radius of an atom A in its ground state which corresponds to the maximum of the radial function for the outer electronic shell of A. For example, in the case of the hydrogen atom, $R_o(H)$ is the Bohr radius which is calculated theoretically and also evaluated from spectral measurements. The values of R_o for 120 atoms were calculated from the solution of Dirac–Fock equations by Declaux [8] with a satisfactory accuracy.

(2) R_e is the distance AA with the particular equilibrium distance, $R_e^{di}(AA)$, for the ground state of the gaseous molecule A_2. R_e is, of course, less than $2R_o$ due to compression of the atoms when the chemical bond is established.

$\chi_{SI}^{di}(A)$ is the relative chemical potential of an atom A in the molecular system A_2, normalized to the chemical potential of Li in gaseous Li_2 [9,10]. The value of $\chi_{SI}^{di}(A)$ is determined from the dissociation energy $D_o(AA)$ and the bond length $R_e^{di}(AA)$.

All these considerations can be transferred to heteronuclear bonds AB. The general equation of STT for the energy of the bond between atoms A and B in a compound is [9]

$$D_o(AB) = k\theta_A\theta_B = k\exp[\chi_{SI}^{di}(A) + \chi_{SI}^{di}(B) + \gamma_A(AB) + \gamma_B(AB)] \tag{6}$$

with

$$\chi_{SI}^{di}(A) + \chi_{SI}^{di}(B) = \chi_{SI}^{di}(AB)\exp(R_e - R_e^{di})(R_e + R_e^{di})^{-1} \tag{7}$$

$$\gamma_A(AB) = (R_o^2(A) - (R_e^{di})^2)(R_o(A)R_e^{di})^{-1} \tag{8}$$

$$\gamma_B(AB) = (R_o^2(B) - (R_e^{di})^2)(R_o(B)R_e^{di})^{-1} \tag{9}$$

where R_e and R_e^{di} are the equilibrium distances between A and B in the compound and in the gaseous diatomic molecule AB, respectively, and $\chi_{SI}^{di}(AB)$ is a constant parameter for the AB bond. In the majority of cases, $\chi_{SI}^{di}(AB)$ can be deduced from two experimental data, the dissociation energy $D_o^{di}(AB)$ and the equilibrium distance AB of the gaseous molecule AB in its ground state, $R_e^{di}(AB)$.

The two main steps to calculate $\Sigma_j D_{o,j}$ for all interactions between atoms in the valent-approximation are the calculation of $\chi_{SI}^{di}(AB)$ and the analysis of the structural data of the studied compound to have all the $R_e(AB)$ values. The value of $\Sigma_j D_{o,j}$ allows to evaluate the enthalpy of formation of the compound under consideration and further to evaluate other thermodynamic parameters related to the enthalpy of formation.

STT has been checked. For instance it gives for the energy of the La–O bonds in $La(OH)_3$ the value 1852 kJ mol^{-1}, the experimental value being 1785.9±40 kJ mol^{-1}.

In the next sections, application of STT to calculate the energies of the bonds Ln–O(nitrato), Ln–O(L) and Ln–O(water) in Ln nitrato malonamide solvates, as well as the enthalpies of formation and of extraction of Ln by malonamide are given. All the calculations are based on X-ray structural investigations on monocrystals [3,6].

2.2. Compounds $Ln(NO_3)_3L_2$

2.2.1. $La(NO_3)_3L_2$ ($L=[(C_2H_5)_2NCO]_2CH_2$)

2.2.1.1. Sum of the bond energies

The gas phase molecule LaO(g) in the ground state $^2\Sigma^+$ is the reference for application of STT. The used parameters are: $R_e^{di}(LaO) = 1.826$ Å, $D_o^{di}(LaO(g)) = 801.17 \pm 4$ kJ mol^{-1} [12]. According to Ref. [8], $R_o(La) = 2.106$ Å and $R_o(O) = 0.4628$ Å, it follows:

$$\gamma_{La}(LaO) = R_o^2(La) - (R_e^{di})^2)(R_o(La)R_e^{di})^{-1} = 0.2830$$

$$\gamma_O(LaO) = (R_o^2(O) - (R_e^{di})^2)(R_o(O)R_e^{di})^{-1} = -3.6924$$

and

$$\chi_{SI}^{di}(LaO) = 5.5225.$$

In the compound $LaL_2(NO_3)_3$ under consideration, the coordination number (CN) of La is CN = 10 and not only all nitrato groups but both ligands L have unequivalent distances La–O [4]. In the triclinic structure of the complex with the space group P1 there are two molecules in the asymmetric unit with two equivalent L molecules. However, these equivalent L molecules have unequivalent distances in the 10-coordinated polyhedra. Thus, the La–O(L) distances for two independent positions are (in Å) 2.44 and 2.51 or 2.45 and 2.54. The values of D_o(La–O(L)) in $La\{(C_2H_5)_2NCO)_2\}_2(NO_3)_3$, *c*, are given, according to the distances La–O, in Table 1. The $\Sigma_1^{10} D_o$(La–O,c) values are 1917.68 and 1868.16 kJ mol^{-1}, respectively, for the first and second molecules $LaL_2(NO_3)_3$ in the

Table 1
Interatomic distances R_e(La–O) (Å) for two molecules in the unit cell of the crystal $LaL_2(NO_3)_3$ ($L=[(C_2H_5)_2NCO]_2CH_2$) [6] and the calculated bond energies (kJ mol^{-1})

No. of La–O bond	R_e(LaO)	D_o(La–O,c)	R_e(LaO)	D_o(La–O,c)
1[a]	2.44 (1)	262.09	2.51 (1)	231.27
2[a]	2.45 (1)	257.45	2.54 (1)	219.20
3[a]	2.57 (2)	207.75	2.56 (2)	211.50
4[a]	2.57 (1)	207.75	2.57 (2)	207.75
5[b]	2.59 (1)	200.45	2.61 (1)	193.40
6[b]	2.64 (2)	183.29	2.63 (2)	186.60
7[b]	2.67 (1)	173.70	2.68 (1)	170.61
8[b]	2.70 (2)	164.60	2.74 (2)	153.90
9[b]	2.83 (2)	130.30	2.74 (2)	153.90
10[b]	2.83 (1)	130.30	2.79 (2)	140.03

[a] La–O(L) bond.
[b] La–O(nitrato) bond.

unit cell. The difference in energy is about 50 kJ mol^{-1}. The average value of $\Sigma_1^{10} D_o$(La–O,c) is 1892.21 kJ mol^{-1} and the uncertainty is no more than 20 kJ mol^{-1} (1%).

In these calculations, the non-valent bond energies Ln–N(nitrato) have not been taken into account as mentioned. Nevertheless, in the frame of STT, for three nitrato groups ΣD_o (La–N(nitrato)) is about 100 kJ mol^{-1}. This value comes from the average distance R_e(La–N)=2.97 Å, R_e^{di}(La–N,g)=2.05 Å, D_o(La–N,g)=420 kJ mol^{-1} [11], R_o(N)=0.5389 Å [8] which give χ_{SI}^{di}(LaN)=4.4729 and D_o(La–N(nitrato))=30 kJ mol^{-1}. Finally, $\Sigma_1^{13} D_o$(La–O,N,c)=1892.21+100=1992.21 kJ mol^{-1}.

2.2.1.2. Enthalpy of formation

The value $\Sigma_1^{13} D_o$(La–O,N,c) is equal to the standard enthalpy of the reaction:

$$La(g) + 2L(c) + 3NO_3^o(c) = LaL_2(NO_3)_3,c \tag{10}$$

and it is close to the standard enthalpy of the reaction:

$$La(g) + 2L(g) + NO_3^o(g) = LaL_2(NO_3)_o,g \tag{11}$$

as shown in Appendix A. It allows to calculate the standard enthalpy of formation of $LaL_2(NO_3)_3$ in the gaseous and the solid state from the equations:

$$\Delta H_f^o(LaL_2(NO_3)_3,g) = \Delta H_{sub}^o(La) + 2\Delta H_f^o(L,g) + 3\Delta H_f^o(NO_3^o),g) - \Sigma D_o(La - O,N,c) \tag{12}$$

$$\Delta H_f^o(LaL_2(NO_3)_3,c) = \Delta H_f^o(LaL_2(NO_3)_3,g) - \Delta H_{sub}^o(LaL_2(NO_3)_3,c) \tag{13}$$

as shown again in Appendix A.

The enthalpy of formation of gaseous L, calculated using AM1 and MNDO models in optimising the geometry of the molecule, is $\Delta H_f^o(L,g) = -(359\pm20)$ kJ mol^{-1}. The values $\Delta H_f^o(NO_3^o,g)=64.5$ kJ mol^{-1} [13] and $\Delta H_{sub}^o(La)=$ 431.37 kJ mol^{-1} [14] have been used. The enthalpy of formation of gaseous radical NO_3^o,g is calculated from:

$$\Delta H_f^o(NO_3^o,g) = \Delta H_f^o(NO_3^-,g) + A(NO_3^o,g) = 64.5\ \text{kJ mol}^{-1} \tag{14}$$

with $\Delta H_f^o(NO_3^-,g) = -(334.6\pm15)$ kJ mol^{-1}, and an electronic affinity, $A(NO_3^o)=(398.1\pm21)$ kJ mol^{-1}, both being average values of several measurements. The enthalpy of sublimation $\Delta H_{sub}^o(LaL_2(NO_3)_3)$ is thought to depend only on the interaction between the organic ligands. It can be evaluated to 120–130 kJ mol^{-1} [13]. Thus, finally, $\Delta H_f^o(LaL_2(NO_3)_3,g) = -2085$ kJ mol^{-1} and $\Delta H_f^o(LaL_2(NO_3)_3,c) = -2205$ kJ mol^{-1}.

A significant parameter for the understanding of the extraction mechanism of Ln nitrates by L is the ratio η between the averaged sum of the bond energies D_o(La–O(L)) and D_o(La–O(nitrato)) for the bidentate ligands:

$$\eta = \frac{D_o(La - O(L))}{D_o(La - O(nitrato))} = 1.24 \tag{15}$$

The organic ligands are stronger bonded with the cation than the nitrato groups are. The difference is about 60 kJ mol^{-1}. If there is not any steric hindrance, the organic ligand L must substitute the nitrato groups. This means, firstly, that the formation of anionic complexes $La(NO_3)_4^-$ or $La(NO_3)_5^{2-}$ in the organic phase is not thermodynamically driven in the presence of L and, secondly, that the coordinative extraction mechanism operates at low concentrations of nitric acid as experimental results show.

2.2.1.3. Enthalpy of extraction of La

The enthalpy of formation of $LaL_2(NO_3)_3$,g allows to evaluate the enthalpy of extraction of La, ΔH_{ext}^o, according to the reaction (1) with $n=2$ from which:

$$\Delta H_{ext}^o = \Delta H_f^o(LaL_2(NO_3)_3,org) - \Delta H_f^o(La^{3+},aq) - 3\Delta H_f^o(NO_3^-,aq) - 2\Delta H_f^o(L,org) \tag{16}$$

with:

$$\Delta H_f^o(LaL_2(NO_3)_3,org) = \Delta H_f^o(LaL_2(NO_3)_3,g) + \Delta H_{solv}^o(LaL_2(NO_3)_3,g) \tag{17}$$

where $\Delta H_{solv}^o(LaL_2(NO_3)_3,g)$ is the enthalpy of solvation of gaseous $LaL_2(NO_3)_3$ molecule. According to the considerations developed by Marcus [17] for the solvation of $UO_2(NO_3)_2$ 2TBP we take as an approximation:

$$\Delta H_{solv}^o(LaL_2(NO_3)_3,g) = 2\Delta H_f^o(L,org) - 2\Delta H_f^o(L,g) \tag{18}$$

which leads to:

$$\Delta H^{o}_{ext} = \Delta H^{o}_{sub}(La) + 3\Delta H^{o}_{f}(NO^{o}_{3},g) - \Sigma D_{o}(La - O,N,c) - \Delta H^{o}_{f})(La^{3+},aq) - 3\Delta H^{o}_{f}(NO^{-}_{3},aq) \quad (19)$$

With $\Delta H^{o}_{f}(La^{3+},aq) = -709.4$ kJ mol^{-1} and $\Delta H^{o}_{f}(NO^{-}_{3},aq) = -206.85$ kJ mol^{-1}, it follows $\Delta H^{o}_{ext} = -37.2 \pm 20$ kJ mol^{-1}. Owing to the accepted approximations, we consider ΔH^{o}_{ext} as an effective extraction enthalpy. In [4] the values of the thermodynamic parameters of extraction of La^{3+} by *N,N′*-dimethyl, *N,N′*-dibutyl malonamide are $\Delta H^{o}_{ext,298} = -18.7 \pm 4.20$ kJ mol^{-1} and $\Delta G^{o}_{ext,298} = -7.5 \pm 0.3$ kJ mol^{-1}. Consequently, we can conclude that experimental and STT evaluated values of the extraction enthalpy are comparable.

2.2.2. $Nd(NO_3)_3L_2$ ($L = CH_2(CONCH_3C_6H_{11})_2$)

The compound of Nd, with CN = 10, is characterized by a large volume owing to the presence of cyclohexyl groups. We have calculated the bond energies D_o(Nd–O,c) corresponding to the measured interatomic distances R_e(Nd–O) in Ref. [3]. The measured distances and the calculated bond energies are given in Table 2. The following initial parameters: R^{di}_{e}(Nd–O) = 1.81 Å, D^{di}_{o}(Nd–O) = 702.91 kJ mol^{-1}, giving χ^{di}_{SI}(Nd–O) = 5.3318 and R_o(Nd) = 2.1116 Å have been used in the calculations.

The ratio between the average sum of the bond energies D_o(Nd–O(L)) and D_o(Nd–O(nitrato)) for the bidentate ligands is in this case:

$$\eta = \frac{D_o(Nd - O(L))}{D_o(Nd - O(nitrato))} = 1.20 \quad (20)$$

The increase of the volume of the organic ligand from ethyl to cyclohexyl (even if two ethyl groups are replaced by two methyls) leads to the decrease of η in comparison with that for the complex $La\{(C_2H_5)_2NCO]_2CH_2\}_2(NO_3)_3$. The trend seems to be that the sum of the bond energies of La with nitrato groups become equal to that with chelating ligands L when the volume of the ligand L increases and that the (Ln–O(L)) bonds are weakened.

Table 2
Interatomic distances R_e(Nd–O) (Å) in the unit cell of crystal $Nd(NO_3)_3L_2$ ($L = CH_2(CONCH_3C_6H_{11})_2$) [3] and calculated bond energies (kJ mol^{-1})

N of Nd–O bond	R_e(Nd–O)	D_o(Nd–O,c)
1[a]	2.462 (10)	208.56
2[a]	2.476 (9)	203.29
3[a]	2.490 (9)	198.16
4[a]	2.512 (10)	190.35
5[b]	2.547 (13)	178.56
6[b]	2.573 (13)	170. 27
7[b]	2.67 (12)	173.70
8[b]	2.641 (13)	150.37
9[b]	2.605 (13)	138.74
10[b]	2.82 (2)	108.30

[a] Nd–O(L) bonds.
[b] Nd–O(nitrato) bond.

According to data of Table 2 and taking into account the correction due to Do(L–N(nitrato)), ΣD_o(Nd–O,N,c) = 1800 kJ mol^{-1}, the enthalpy of the extraction of Nd can be calculated as follows:

$$\Delta H^{o}_{ext} = \Delta H^{o}_{sub}(Nd) + 3\Delta H^{o}_{f}(NO^{o}_{3},g) - \Sigma D_{o}(Nd - O,N,c) - \Delta H^{o}_{f}(Nd^{3+}aq) - 3\Delta H^{o}_{f}(NO^{-}_{3}aq) \quad (21)$$

which gives with ΔH^{o}_{sub}(Nd) = 328.48 kJ mol^{-1} and $\Delta H^{o}_{f}(Nd^{3+}aq) = -695.5$ kJ mol^{-1}, $\Delta H^{o}_{ext} = (39 \pm 30)$ kJ mol^{-1}. The decrease of the bond energy Nd–O reduces the extraction ability. This qualitative conclusion is in line with a decreasing value of η.

2.3. Compounds $Nd(NO_3)_3(H_2O)_mL$

The aim of this section is to look at some general trends in Ln–O bond energies due to the decrease of the number of diamide ligands within the complexes.

2.3.1. $Nd(NO_3)_3(H_2O)_2L$ ($L = (C_6H_5CH_3NCO)_2CH_2$)

In Table 3, the interatomic distances R_e(Nd–O) [3] together with the calculated bond energies D_o(Nd–O) are given. The average bond energy D(Nd–O(L)) is 214.36 kJ mol^{-1}. In comparison with the complex $Nd(NO_3)_3L_2$ ($L = (CONCH_3C_6H_{11})_2CH_2$), the bond energy D_o(Nd–O(L)) increases on 28.5 kJ mol^{-1}. The average bond energy D_o(Nd–O(nitrato)) is 154.44 kJ mol^{-1}. The sum of the average bond energy is ΣD_o(Nd–O) = 1695.5 kJ mol^{-1}. In comparison with the complex $Nd(NO_3)_3L_2$ ($L = (CONCH_3C_6H_{11})_2CH_2$), the coefficient η increases significantly. The ratio between the sum of average bond

Table 3
Interatomic distances R_e(Nd–O) (Å) for two molecules in the unit cell of crystal $Nd(NO_3)_3$ $(H_2O)L$ ($L = (C_6H_5CH_3NCO)_2CH_2$) [3] and calculated bond energies (kJ mol^{-1})

N of Nd–O bond	R_e(Nd–O)	D_o(Nd–O,c)	R_e(Nd–O)	D_o(Nd–O,c)
1[a]	2.428 (8)	221.93	2.398 (7)	234.43
2[a]	2.477 (8)	202.92	2.490 (8)	198.16
3[c]	2.541 (9)	180.53	2.581 (8)	167.80
4[c]	2.580 (9)	168.11	2.594 (9)	163.87
5[b]	2.595 (8)	163.57	2.575 (9)	169.65
6[b]	2.600 (9)	162.08	2.617 (9)	157.11
7[b]	2.610 (9)	159.14	2.618 (9)	156.83
8[b]	2.617 (9)	157.11	2.637 (9)	151.48
9[b]	2.630 (9)	153.43	2.672 (10)	142.08
10[b]	2.699 (9)	142.86	2.688 (8)	137.97

[a] Nd–O(L) bond.
[b] Nd–O(nitrato) bond.
[c] Nd–O(water) bond.

energies D_o(Nd–O(L)) and D_o(Nd–O(nitrato)) for the bidentate ligands is:

$$\eta = \frac{D_o(\mathrm{Nd}-\mathrm{O(L)})}{D_o(\mathrm{Nd}-\mathrm{O(nitrato)})} = 1.25 \qquad (22)$$

The bond energies Nd–O in the two compounds with one and two chelating ligands can be used to discuss some interesting features of the interrelation between the stereochemistry and the bond energy. The ratio $\eta[Nd(NO_3)_3(H_2O)L]$ (with $L=(C_6H_5CH_3NCO)_2CH_2$) is equal to $\eta[La(NO_3)_3L_2]$ (with $L=[(C_2H_5)_2NCO]_2CH_2$) although D_o(La–O)$>$$D_o$(Nd–O). On the other hand, $\eta[Nd(NO_3)_3(H_2O)L]$ (with $L=(C_6H_5CH_3NCO)_2CH_2$)$>$ $\eta[Nd(NO_3)_3L_2]$ (with $L=CH_2(CONCH_3C_6H_{11})_2$). From the comparison of the La compound with the Nd compound we note that in both compounds with Nd the bond energies D_o(Nd–O(L)) change more significantly than those of D_o(Nd–O(nitrato)). So, one can see that the increase (decrease) of the steric effect between ligands in the coordination sphere of the metal results in the decrease (increase) of the bond energies. We propose to call this effect the 'Fid-effect'.

2.3.2. $Yb(NO_3)_3(H_2O)L$ ($L=(C_6H_5CH_3NCO)_2CH_2$)

The difference in the Ln ionic radii of Nd, Er and Yb is reflected both in the lattice parameters of similar compounds and the CN of Ln. Yb appears to have CN = 9 in the compound $Yb(NO_3)_3(H_2O)L$, with $L=(C_6H_5CH_3NCO)_2CH_2$. In Table 4 the measured interatomic distances R_e(Yb–O) versus the calculated bond energies D_o(Yb–O) are given. We have used the following parameters for the calculation of all the D_o(Yb–O): R_e^{di}(Yb–O) = 1.807 Å, D_o^{di})(Yb − O) = 397.48 kJ mol^{-1} and R_o(Yb) = 1.843 Å, which give χ_{SI}^{di}(Yb − O) = 5.0247. The average bond energy D_o(Yb–O(nitrato)) and D_o(Yb–O(L)) are 112.49 and 155.54 kJ mol^{-1}, respectively. The ratio between the average sum of the bond energies D_o(Yb–O(L)) and D_o(Yb–O(nitrato)) for the bidentate ligands is $\eta = 1.2$. Thus, the ratio η decreases in comparison with the similar compound of Nd. This corresponds to the increase of the strain in the complex of Yb. The average sum of the bond energy is ΣD_o(Yb–O) = 1124.1 kJ mol^{-1}.

Table 4
Interatomic distances R_e(Yb–O) (Å) in the crystal $Yb(NO_3)_3(H_2O)L$ ($L=(CH_3C_6H_5CON)_2CH_2$) [3] and the calculated bond energies (kJ mol^{-1})

N of Yb–O bond	R_e(Yb–O)	D_o(Yb–O,c)
1[a]	2.274 (6)	159.14
2[a]	2.296 (8)	152.54
3[c]	2.350 (8)	137.49
4[b]	2.396 (8)	125.84
5[b]	2.447 (8)	114.09
6[b]	2.460 (8)	111.28
7[b]	2.474 (9)	108.32
8[b]	2.474 (9)	108.32
9[b]	2.473 (7)	108.53

[a] Yb–O(L) bond.
[b] Yb–O(nitrato) bond
[c] Yb–O(water) bond.

2.3.3. $Er(NO_3)_3(H_2O)L$ ($L=(C_6H_5CH_3NCO)_2CH_2$)

The compounds $Ln(NO_3)_3(H_2O)L$ (Ln = Er, Yb), are isomorphic [3]. Moreover, the interatomic distances Ln–O in both complexes are near to each other. One can compare the average distances Yb–O (Table 4) with those of Er–O [15] given for similar complexes of Er: R_e(Er–O(nitrato)) = 2.407 Å, R_e(Er–O(L)) = 2.297 Å. For the interatomic distance Er–O(water) we have accepted 2.35 Å. The following initial parameters for the calculation of D_o(Er–O) have been used: R_e^{di}(Er–O) = 1.795 Å [16], D_o^{di}(Er–O) = (606.7 ± 12.5) kJ mol^{-1}, R_o(Er) = 2.0223 Å which gives χ_{SI}^{di}(ErO) = 5.2204. The average bond energies for the compound $Er(NO_3)_3(H_2O)L$ are D_o(Er–O(nitrato)) = 190.5 kJ mol^{-1}, D_o(Er–O(L)) = 233.67 kJ mol^{-1} and D_o(Er–O(water)) = 211.74 kJ mol^{-1} which give ΣD_o(Er–O) = 1922.1 kJ mol^{-1}. The index of strain of the compound is $\eta = 1.13$. The position of the element in the Ln series determines the strain of diamide compound.

3. Conclusion

The evaluations of thermodynamic parameters of nitrato compounds of Ln with malonamide based on the X-ray data of crystallized compounds show that the bidentate chelating ligand has an energy advantage over the NO_3^- anion and over H_2O. The effect results in a coordinative mechanism for the extraction of Ln from nitric acid solutions of which concentrations are below 1 mol dm^{-3}.

The steric effect of ligands as well as their volumes have a significant influence for the geometry of the coordination sphere. The existence of a 'Fid-effect' for the Ln nitrato compounds with malonamide is shown; a larger volume of a ligand L decreases the bond energies Ln–O(L) and Ln–O(nitrato). In principle, the 'Fid-effect' can lead to the adequation of the bond energies Ln–O(L) and Ln–O(nitrato).

Across the lanthanide series, the 4f shell is progressively filled. In the beginning of the series there is some covalent interaction between Ln 4f atomic orbitals and their surroundings. Besides, the excited 5d and 6s orbitals have a significant contribution for covalent bonding. For the heavy Ln elements, the 4f atomic orbitals are highly contracted and have only a small overlapping with 2s and 2p oxygen orbitals. The excitation energies $4f^q$–$4f^{q-1}5d$ or $4f^q$–$4f^{q-1}6s$ sharply increase in the heavy lanthanides. The strong localization of 4f electrons decreases the bond energy Ln–O when one passes from the light to the heavy elements (if the complexes of same composition across the series are considered). This regularity is demonstrated for the nitrato complexes of Ln with malonamides.

Besides the general regularities in the trend of the bond energies of Ln–O(L), Ln–O(nitrato) and Ln–O(water) across the lanthanide series, we have shown a more specific regularity based on the tetrad effect which will be discussed in an other forthcoming paper.

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Appendix A

Considerations on the enthalpies of formation

The values of ΣD_o(La–O,N,c) calculated according to STT correspond to the molar process which bring together one atomic La, two L molecules and one nitrato group with bond lengths corresponding to the solid state:

$$\mathrm{La(g)} + 2\mathrm{L(c)} + 3\mathrm{NO_3^o(c)} = \mathrm{LaL_2(NO_3)_3,c}; \quad \Sigma D_o(\mathrm{La} - \mathrm{O,N,c}) \tag{A1}$$

The enthalpy of formation of this compound, $\Delta H_f^o(\mathrm{LaL_2(NO_3)_3,c})$, is defined according to the reaction between all the elements in their standard state:

$$\Sigma\ \mathrm{elements} = \mathrm{LaL_2(NO_3)_3,c} \tag{A2}$$

According to Eq. (A1) and Eq. (A2) it follows:

$$\Delta H_f^o[\mathrm{LaL_2(NO_3)_3,c}] = \Delta H_{\mathrm{sub}}^o(\mathrm{La}) + 2\Delta H_f^o(\mathrm{L,c}) + 3\Delta H_f^o(\mathrm{NO_3^o,c}) - \Sigma D_o(\mathrm{La} - \mathrm{O,N,c}) \tag{A3}$$

but $\Delta H_f^o[\mathrm{LaL_2(NO_3)_3,c}]$ cannot be calculated because, at least, $\Delta H_f^o(\mathrm{NO_3^o,c})$ is not known. What are known, are the enthalpies of formation of L and $\mathrm{NO_3^o}$ in gaseous phase. So, from the three following processes:

$$\mathrm{La(g)} + 2\mathrm{L(g)} + 3\mathrm{NO_3^o(g)} = \mathrm{LaL_2(NO_3)_3,g}; \quad \Sigma D_o(\mathrm{La} - \mathrm{O,N,g}) \tag{A4}$$

$$\Sigma\ \mathrm{elements} = \mathrm{LaL_2(NO_3)_3,g}; \quad \Delta H_f^o[\mathrm{LaL_2(NO_3)_3,g}] \tag{A5}$$

$$\mathrm{LaL_2(NO_3)_3,c} = \mathrm{LaL_2(NO_3)_3,g}; \quad \Delta H_{\mathrm{sub}}^o[\mathrm{LaL_2(NO_3)_3,c}] \tag{A6}$$

one gets from Eq. (A4) and Eq. (A5):

$$\Delta H_f^o[\mathrm{LaL_2(NO_3)_3,g}] = \Delta H_{\mathrm{sub}}^o(\mathrm{La}) + 2\Delta H_f^o(\mathrm{L,g}) + 3\Delta H_f^o(\mathrm{NO_3^o,g}) - \Sigma D_o(\mathrm{La} - \mathrm{O,N,g}) \tag{A7}$$

and from Eq. (A5) and Eq. (A6):

$$\Delta H_f^o[\mathrm{LaL_2(NO_3)_3,c}] = \Delta H_f^o[\mathrm{LaL_2(NO_3)_3,g}] - \Delta H_{\mathrm{sub}}^o[\mathrm{LaL_2(NO_3)_3,c}] \tag{A8}$$

Now, to calculate $\Delta H_f^o[\mathrm{LaL_2(NO_3)_3,g}]$ one needs at least ΣD_o(La–O,N,g), which is, according to STT, different from ΣD_o(La–O,N,c) because length of the bonds differ slightly in solid and gaseous states. The difference is given, using Eq. (A8), Eq. (A7) and Eq. (A3), by:

$$\Sigma D_o(\mathrm{La} - \mathrm{O,N,g}) - \Sigma D_o(\mathrm{La} - \mathrm{O,N,c}) = 2\Delta H_{\mathrm{sub}}^o(\mathrm{L,c}) + 3\Delta H_{\mathrm{sub}}^o(\mathrm{NO_3^o,c}) - \Delta H_{\mathrm{sub}}^o[\mathrm{LaL_2(NO_3)_3,c}] \tag{A9}$$

taking into account the definition of sublimation energies of compounds.

The second member of Eq. (A9) is close to zero because the interactions between L and $\mathrm{NO_3^o}$ groups are much less than all the others, either in the solid and the gaseous states. So, the energy needed to separate isolated clusters of $\mathrm{LaL_2(NO_3)_3}$ or separated L and $\mathrm{NO_3^o}$ groups are close. Accordingly, the approximation:

$$\Sigma D_o(\mathrm{La} - \mathrm{O,N,g}) = \Sigma D_o(\mathrm{La} - \mathrm{O,N,c})$$

seems valid.

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