

Chemical speciation of polynuclear complexes containing $[\text{Ln}_2\text{M}_3\text{L}_6]$ units^{*,**}

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Abstract: Polynuclear complexes are widely regarded as potential materials in separation, catalysis, gas storage, and molecular recognition. Those complexes including lanthanide (Ln) ions in the heterobimetallic assembly enhance the structural flexibility and increase the thermodynamic stability. Up to now, the studies on these heteropolynuclear complexes have been mostly focused on lanthanide-copper compounds in the solid state. We have expanded the studies to solution chemistry, to know if such polynuclear species can also exist in aqueous solution. In this work, potentiometric titrations (25.0 °C, and $I = 0.50 \text{ M Me}_4\text{NCl}$) were carried out for systems containing a Ln ion (La, Ce, Sm), a bridging ligand (oda or ida), and a second metal ion. We found that polynuclear units can be formed with M^{II} (Mn, Fe, Co, Ni, Cu, Zn, Cd, and VO^{2+}) and M^{III} (Fe, Al) ions, and can be predominant in aqueous solution. Species like $[\text{Ln}_2\text{M}_3\text{L}_6]$ or $[\text{Ln}_2\text{M}_3\text{L}_6(\text{OH})_n]^{n-}$ ($n = 3, 6$) can exist in solution, representing the same 2:3:6 stoichiometry found in the solid state. The presence of an amino group in the ida ligand makes the mononuclear complexes with 3d metal ions more stable, preventing to some extent the formation of polynuclear complexes.

Keywords: speciation; potentiometry; polynuclear compounds; lanthanide; stability constants.

INTRODUCTION

The design and building of metal coordination polymers containing lanthanide (Ln) ions and *d*-metal ions have attracted great interest during the last 10 years. They have found applicability in the areas of supramolecular and materials chemistry. For example, the presence of the Ln^{III} introduces fascinating luminescent properties. Consequently, they have been used as metal ion sensors in solution [1–5]. In the solid state, the use of polymers containing *f* and *d* metal centers in a mixed-metal system leads to a broad palette of structural motifs [6,7]. The construction of 3D coordination polymers with well-defined pores is of great interest for the development of zeolite-type materials to be applied in catalysis, gas storage, chemical separation, and ion exchange processes. Those materials exhibiting a high thermal stability and available Lewis acid metal sites (usually coordinated water) are of particular relevance [8]. Heterobimetallic complexes have been proved to be efficient catalysts to carry out very specific reactions [9]. An important group of such polymers is based on the flexible ligands H_2oda (2,2'-oxydiacetic acid) or H_2ida (iminodiacetic acid). The structure of these ligands is shown in Fig. 1. They are

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**Ln: lanthanide ion; M: 3d metal ion; L: oxydiacetate, iminodiacetate

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dicarboxylic ligands with an extra donor group. Oda is a pure O-donor, while ida is a N/O-donor. The denticity is three for both, the central coordinating atom being the only difference. This slight change results in very interesting consequences both in the structure and in the overall stability of the polynuclear complexes. The ligand oda has proved to bridge Ln^{III} and Cu^{II} with the formation of polynuclear complexes in the solid state. The structures $[\text{Ln}_2\text{Cu}_3(\text{oda})_6(\text{H}_2\text{O})_6]$ ($\text{Ln} = \text{Er}, \text{Yb}$) [10,11], $[\text{Ln}_2\text{Cu}_3(\text{oda})_6(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}, \text{Gd}$) [10,12], $[\text{Sm}_2\text{Cu}_3(\text{oda})_6(\text{H}_2\text{O})_6] \cdot 6.5\text{H}_2\text{O}$ [13], $[\text{Ln}_2\text{Cu}_3(\text{oda})_6(\text{H}_2\text{O})_6] \cdot 12\text{H}_2\text{O}$ ($\text{Ln} = \text{Y}, \text{Pr}, \text{Nd}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}$) [14–16], and $[\text{Ln}_2\text{Cu}_3(\mu_2\text{-H}_2\text{O})(\text{oda})_6(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Ce}$) [17], have been reported. In the isostructural compounds $[\text{Ln}_2\text{Cu}_3(\text{oda})_6(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}$, the Ln metal ion is nine-coordinated, being surrounded by nine oxygen atoms belonging to three oda ligands. The most interesting point in the structures is the formation of a 3D network containing large hexagonal channels (Fig. 2). The channels contain the lattice water molecules. All the complexes Ln-oda-Cu can be thought of as being formed by $[\text{Ln}(\text{oda})_3]$ building blocks, assembled by the presence of Cu ions which connect the blocks in a supramolecular structure. The unique reported structure of a polynuclear complex with oda containing another metal ion instead of Cu is the $[\text{La}_2\text{Co}_3(\text{oda})_6(\text{H}_2\text{O})_6]$ [18].

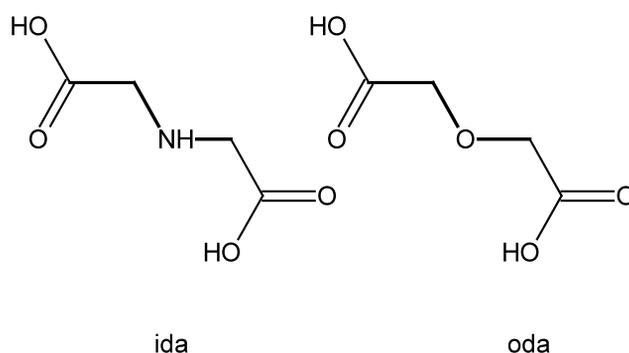


Fig. 1 Schematic structure of the ligands oda and ida.

The change from oda to ida as ligand, i.e., the substitution of an O-donor by a N-donor atom, provokes a great change in the structure of the polynuclear complexes. The structure is now based on $[\text{Cu}(\text{ida})_2]$ blocks linked by Ln^{III} ions. The isostructural complexes $[\text{Ln}_2\text{Cu}_3(\text{ida})_6] \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$) [19–24] are also known. Each unit $[\text{Cu}(\text{ida})_2]$ uses the four uncoordinated oxygen atoms to bind Ln^{3+} . The Ln ion is also nine-coordinated, surrounded by nine carboxylic oxygen atoms from six neighboring ida ligands. Hexagonal channels are formed again, even though they are smaller (Fig. 2). They run along the crystallographic *c* axis and house the lattice water molecules.

Once the solid-state structure of these polynuclear assemblies has been studied, it would be very interesting to know if they can also exist in solution. The presence of similar molecular arrangements in aqueous solution would allow one to assay the complexes as potential homogeneous catalysts for many processes. With this in mind, we have previously reported the formation of polynuclear species containing Ln ions (Sm and La) and various metal ions bridged by oda [13,18]. In this work, we extend this study to Ce-M-oda systems and to those polynuclear complexes which include ida as bridging ligand.

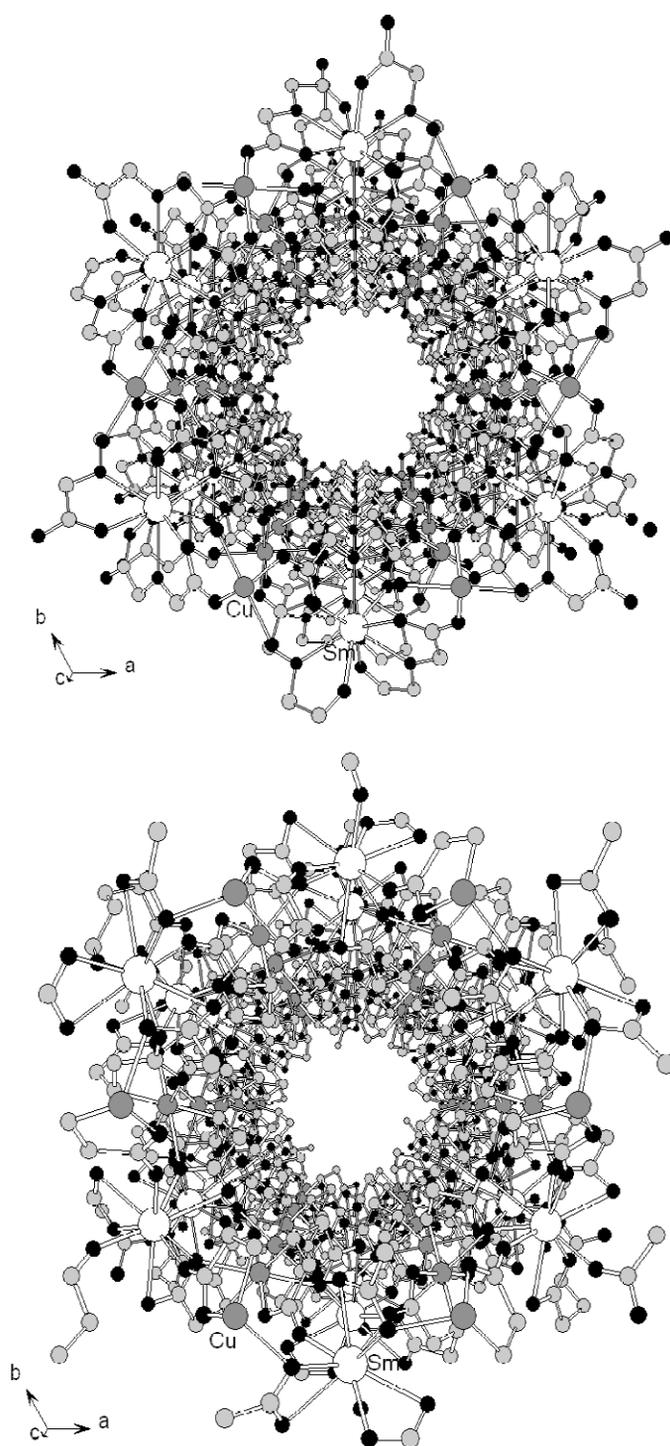


Fig. 2 Channeled structure of $[\text{Sm}_2\text{Cu}_3(\text{oda})_6(\text{H}_2\text{O})_6]$ (top) and $[\text{Sm}_2\text{Cu}_3(\text{ida})_6]$ (bottom) viewed down the crystallographic *c*-axis. Crystallization water molecules and H atoms are omitted for clarity.

EXPERIMENTAL

Acidic solutions of the metal ions were prepared from commercial salts and standardized according to standard techniques [25–27]. All the solutions were freed of carbon dioxide by boiling the solvent and subsequent cooling under Ar atmosphere. The standard HCl solution was prepared from Merck standard ampoules. The titrant solution [0.1 M solution of $\text{Me}_4\text{N}(\text{OH})$ in 0.50 M Me_4NCl] was prepared by dissolving $\text{Me}_4\text{N}(\text{OH})\cdot 5\text{H}_2\text{O}$ (Fluka) and standardized with potassium biphthalate. The hydrolysis constants of La^{III} , Sm^{III} , Fe^{II} , Al^{III} , Fe^{III} , and VO^{2+} , under the same conditions of the study, were taken from our previous reports [13,18]. Protonation constants of the ligand oda and the formation constants of $\text{M}^{\text{II}}\text{-oda}$ and $\text{M}^{\text{III}}\text{-oda}$ species were also taken from the same reports. The hydrolysis constant of Ce^{3+} was measured in the same conditions by potentiometry.

The protonation constants of the ligand ida and the formation constants of $\text{M}^{\text{II}}\text{-ida}$ and $\text{M}^{\text{III}}\text{-ida}$ species were measured. The behavior of ida in the presence of M^{II} and M^{III} ions was analyzed through two sets of potentiometric titrations (ca. 100 experimental points for each titration), at metal concentrations ranging from 7 to 20 mM and $\text{M}^{\text{II}}\text{:ida}$ or $\text{M}^{\text{III}}\text{:ida}$ molar ratios 1:1 and 1:3. Then, the formation of the mixed species was tested by at least three other potentiometric titrations with $\text{Sm}:\text{M}:\text{ida}$ molar ratios between 1:1:2 and 2:3:6, and different total concentrations of the components. The Ce-M-oda systems were studied analogously.

In all cases, an accurately known volume of the solutions was added into a 20-mL titration cell. After thermal equilibrium was reached, hydrogen ion concentrations were determined in successive readings, each performed after a small incremental addition of standard 0.1 M $\text{Me}_4\text{N}(\text{OH})$ solution (carried out using a Crison 2031 piston buret). Electromotive force values were recorded with the help of a Radiometer 85 pH meter, using a glass electrode and a calomel reference electrode. The experimental data were collected automatically as previously described [28]. The ionic strength was kept constant throughout the titrations by using solutions containing 0.50 M Me_4NCl and relatively low concentrations of the metal ions. Presaturated argon (free of CO_2) was bubbled through the solutions during titrations to eliminate the effect of atmospheric carbon dioxide, and the temperature was kept at 25.0 (± 0.1) °C. The cell constants E° and the liquid junction potentials were determined by means of a strong acid–base titration using the GLEE program [29]. Data were analyzed using the HYPERQUAD program [30], and species distribution diagrams were produced using the HySS program [31]. The fit of the values predicted by the model to the experimental data was estimated on the basis of the parameter σ , corresponding to the scaled sum of square differences between predicted and experimental values.

RESULTS AND DISCUSSION

Tables 1–5 compile the stability data at 25.0°, $I = 0.50$ M Me_4NCl , for the systems under study, including those obtained in this work and those previously reported.

Table 1 Protonation constants of the ligands oda and ida, and hydrolysis of lanthanide cations (25.0 °C, $I = 0.50$ M Me₄NCl).

Protonation constants of oda	log K	Ref.
$L^{2-} + H^+ \rightarrow HL^-$	3.811(5)	13
$L^{2-} + 2 H^+ \rightarrow H_2L$	6.515(9)	13
Protonation constants of ida		
$L^{2-} + H^+ \rightarrow HL^-$	9.267(3)	a
$L^{2-} + 2 H^+ \rightarrow H_2L$	11.903(6)	
$L^{2-} + 3H^+ \rightarrow H_3L^+$	13.772(8)	
Ln hydrolysis		
$La^{3+} + H_2O \rightarrow [La(OH)]^{2+} + H^+$	-9.3(1)	18
$Ce^{3+} + H_2O \rightarrow [Ce(OH)]^{2+} + H^+$	-5.7(1)	b
$Sm^{3+} + H_2O \rightarrow [Sm(OH)]^{2+} + H^+$	-6.7(1)	32

^aThis work, $\sigma = 1.0$.

^bThis work, $\sigma = 0.2$.

Table 2 Overall formation constants for M-oda and Ln-oda complexes at 25.0 °C, $I = 0.50$ M Me₄NCl.

M-oda complexes	log β_{pqr}									Ref.	
	β_{111}	β_{110}	β_{11-1}	β_{121}	β_{120}	β_{12-1}	β_{12-2}	β_{130}	β_{222}		
Mn ²⁺		2.16(5)							12.6(1)	13	
Fe ²⁺	4.34(8)	2.01(1)								13	
Co ²⁺		2.15(1)							11.7(1)	13	
Ni ²⁺	4.86(3)	2.42(1)								13	
Cu ²⁺	5.67(2)	3.46(1)	-1.14(2)							13	
Zn ²⁺	4.67(5)	3.13(1)								13	
Cd ²⁺		2.14(1)								13	
VO ²⁺	7.6(1)	5.6(1)			7.2(1)	1.3(1)		9.0(1)		13	
Fe ³⁺		4.64(5)	1.92(9)	10.87(6)	8.33(4)		-0.33(8)			13	
Al ³⁺	5.14(6)	2.79(2)	-1.47(3)							13	
Ln-oda complexes											
	β_{110}	β_{120}	β_{13}								
La ³⁺	4.86(1)	8.28(1)	10.29(3)								18
Ce ³⁺	4.8(1)	8.23(1)	10.40(2)								a
Sm ³⁺	5.64(1)	9.62(2)	11.8(2)								13

^aThis work, $\sigma = 0.9$. β_{pqr} (M-oda species) corresponds to the equilibria: $pM^{3+/2+} + qL^{2-} + rH_2O \leftrightarrow [M_p(L)_q(OH)_r]^{(3p-2q-r)/(2p-2q-r)+} + rH^+$ ($r < 0$); $pM^{3+/2+} + qL^{2-} + rH^+ \leftrightarrow [M_pL_qH_r]^{(3p-2q+r)/(2p-2q+r)+}$ ($r > 0$).

Table 3 Overall formation constants for M-ida and Sm-ida complexes at 25.0 °C, $I = 0.50$ M Me₄NCl. β_{pqr} (M-ida species) corresponds to the equilibria: $pM^{3+/2+} + qL^{2-} + rH_2O \leftrightarrow [M_p(L)_q(OH)_r]^{(3p-2q-r)+/(2p-2q-r)+} + rH^+$ ($r < 0$); $pM^{3+/2+} + qL^{2-} + rH^+ \leftrightarrow [M_pL_qH_r]^{(3p-2q+r)+/(2p-2q+r)+}$ ($r > 0$).

	log β_{pqr}									σ
	β_{112}	β_{111}	β_{110}	β_{11-1}	β_{121}	β_{120}	β_{11-2}	β_{220}	β_{22-2}	
Mn ²⁺	12.56(9)	10.34(4)	4.30(1)	-5.73(2)		7.01(1)				0.6
Fe ²⁺		10.54(1)	5.78(1)			10.15(1)				0.5
Co ²⁺		11.246(8)	7.265(9)		17.83(4)	12.853(9)				0.8
Ni ²⁺		11.15(1)	8.48(1)		18.94(5)	15.09(1)				1.0
Cu ²⁺			10.32(1)		20.80(4)	16.18(2)				1.7
Zn ²⁺		7.47(1)	11.20(1)			12.69(2)				1.6
Cd ²⁺		10.84(1)	5.27(1)		16.01(4)	9.09(2)				1.6
VO ²⁺		11.91(2)	9.91(5)	4.44(9)	21.07(1)				11.91(5)	1.7
Fe ³⁺		11.81(9)	11.12(2)		22.78(2)	20.13(2)	5.07(3)			0.8
Al ³⁺		11.24(1)	8.51(1)				-1.24(9)	18.15(8)	11.17(3)	0.9
Sm-ida complexes										
	β_{110}	β_{120}	β_{130}							
Sm ³⁺	5.914(5)	10.230(9)	12.60(6)							0.9

Table 4 Overall formation constants for Ln-M-oda complexes, 25.0 °C, $I = 0.50$ M Me₄NCl. Charges of the species are omitted for clarity. The data for La species were taken from ref. [18], and those for Sm species from ref. [13]. β_{pqr} corresponds to the equilibria: $pLn^{3+} + qM^{2+} + rL^{2-} + sH^+ \leftrightarrow [Ln_pM_qL_rH_s]^{(2r-3p-2q-s)-}$ ($s > 0$); $pLn^{3+} + qM^{2+/3+} + rL^{2-} + sH_2O \leftrightarrow [Ln_pM_qL_r(OH)_s]^{(2r+s-3p-2q)-/(2r+s-3p-3q)-} + sH^+$ ($s < 0$).

Ln	M	Equilibrium formation constant (log β_{pqr})					σ
		$[Ln_2M_3L_6]$	$[Ln_2M_3L_6(OH)_n]$	$[LnML_3]$	$[LnML_3(OH)_n]$	$[LnML_3H_2]$	
Ce	Mn ²⁺			12.18(7)	7.45(6) $n = 1$		1.1
	Fe ²⁺		16.75(7) $n = 3$	13.04(2)			1.6
	Co ²⁺	30.04(6)					2.0
	Ni ²⁺			13.63(2)		19.49(2)	2.0
	Cu ²⁺			13.05(4)		18.09(8)	1.0
	Zn ²⁺	31.81(8)			10.73(3) $n = 1$		2.0
	Cd ²⁺				7.79(4) $n = 1$		0.5
	VO ²⁺	40.12(3)		16.99(3)			2.7
	Fe ³⁺		21.32(4) $n = 6$	18.91(4)	13.66(2) $n = 1$		2.5
Al ³⁺		20.59(9) $n = 3$	13.68(4)	10.97(5) $n = 1$		1.9	
			7.25(7) $n = 6$				
La	Mn ²⁺	30.32(4)	18.40(8) ($n = 3$)				
	Fe ²⁺		17.11(4) ($n = 3$)	12.54(3)			
	Co ²⁺	29.6(2)			7.72(8) ($n = 1$)		
	Ni ²⁺	30.49(5)			8.31(5) ($n = 1$)		
	Cu ²⁺	32.52(6)			11.19(2) ($n = 1$)		
	Zn ²⁺	31.6(1)			9.78(3) ($n = 1$)		
	Cd ²⁺	30.5(1)			8.92(4) ($n = 1$)		
	VO ²⁺			16.15(4)			
	Fe ³⁺	38.00(3)	20.11(4) ($n = 6$)	15.79(3)	13.68(1) ($n = 1$)		
	Al ³⁺		20.49(7) ($n = 3$)	13.33(4)			

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Table 4 (Continued).

Ln	M	Equilibrium formation constant ($\log \beta_{pqrs}$)					σ
		$[\text{Ln}_2\text{M}_3\text{L}_6]$	$[\text{Ln}_2\text{M}_3\text{L}_6(\text{OH})_n]$	$[\text{LnML}_3]$	$[\text{LnML}_3(\text{OH})_n]$	$[\text{LnML}_3\text{H}_2]$	
Sm	Mn ²⁺		24.6(1) ($n = 3$)		11.76(3) ($n = 1$)		
	Fe ²⁺		24.1(1) ($n = 3$)		12.11(3) ($n = 1$)		
	Co ²⁺		23.46(5) ($n = 3$)				
	Ni ²⁺		22.80(6) ($n = 3$)				
	Cu ²⁺		24.60(7) ($n = 3$)				
	Zn ²⁺		24.35(5) ($n = 3$)				
	Cd ²⁺		22.88(7) ($n = 3$)				
	VO ²⁺		38.21(8) ($n = 3$)				
	Fe ³⁺		36.67(3) ($n = 3$)	18.91(4)		14.23(3) ($n = 2$)	
			28.31(5) ($n = 6$)				
	Al ³⁺		22.6(2) ($n = 3$)			10.97(5) ($n = 1$)	
		14.75(5) ($n = 5$)					

Table 5 Overall formation constants for Sm-M-ida polynuclear complexes, 25.0 °C, $I = 0.50$ M Me₄NCl. Charges of the species are omitted for clarity. β_{pqrs} corresponds to the equilibria: $p\text{Sm}^{3+} + q\text{M}^{2+} + r\text{L}^{2-} + s\text{H}^+ \leftrightarrow [\text{Sm}_p\text{M}_q\text{L}_r\text{H}_s]^{(2r-3p-2q-s)-}$ ($s > 0$); $p\text{Sm}^{3+} + q\text{M}^{2+/3+} + r\text{L}^{2-} + s\text{H}_2\text{O} \leftrightarrow [\text{Sm}_p\text{M}_q\text{L}_r(\text{OH})_s]^{(2r+s-3p-2q)-(2r+s-3p-3q)-} + s\text{H}^+$ ($s < 0$).

M	Equilibrium formation constant ($\log \beta_{pqrs}$)										σ
	$[\text{Sm}_2\text{M}_3\text{L}_6]$	$[\text{SmML}(\text{OH})]$	$[\text{SmML}]$	$[\text{SmML}_2]$	$[\text{SmML}_3]$	$[\text{SmML}_3\text{H}]$	$[\text{Sm}_2\text{M}_3\text{L}_6(\text{OH})_3]$	$[\text{SmML}_3(\text{OH})_3]$	$[\text{SmML}_2\text{H}]$	$[\text{SmM}_2\text{L}_3]$	
Mn ²⁺		0.29(4)		12.26(3)					18.69(2)		0.6
Fe ²⁺				7.39(6)							0.9
Co ²⁺	48.48(7)					26.66(5)					1.2
Ni ²⁺	55.07(3)					28.70(3)					0.9
Cu ²⁺	58.65(3)					30.12(2)					0.7
Zn ²⁺			8.19(8)							23.75(2)	1.2
Cd ²⁺	41.41(5)		8.22(5)			24.49(2)					0.8
VO ²⁺	58.22(5)				24.58(2)						1.4
Fe ³⁺	76.54(4)				35.47(2)		69.34(7)	25.92(5)			2.6
Al ³⁺							40.79(4)				2.8

The titration curves of oda and ida (generally labeled as L) show two or three equivalent points respectively. The third protonation is due to the presence of the N-connecting atom. The comparison of $\log K_1$ and $\log K_2$ values (Table 1) shows a higher basic character of the deprotonated ida ligand. This is due to the cumulative effect of basic amino groups and the high negative charge of the carboxylate groups [33].

The hydrolysis of the Ln³⁺ ions in aqueous solution is an unavoidable competitive process that should be considered to have a full description of the systems. Table 1 shows the hydrolysis constants of lanthanides (formation of $[\text{Ln}(\text{OH})]^{2+}$) for La, Ce, and Sm. These constants were taken into account for the following steps of the work.

Thermodynamic stability of lanthanide complexes with oda and ida

The formation of mononuclear species containing oda: $[\text{Ln}(\text{L})]^+$, $[\text{Ln}(\text{L})_2]^-$, and $[\text{Ln}(\text{L})_3]^{3-}$ has been reported for all Ln ions. The last stoichiometry is also the most frequently found in the solid state, as re-

cently reviewed [34]. In all these species, the ligand oda is always coordinated to the metal ions in its fully deprotonated form.

Table 2 shows the $\log \beta_{pqr}$ values for La^{3+} , Ce^{3+} , and Sm^{3+} . The species distribution diagram showing the complexation of samarium(III) with oda is presented in Fig. 3. Very similar diagrams can be obtained for the other Ln ions. Even in the presence of equimolar amounts of the ligand, a relatively high percentage of the metal ion is retained in solution, especially in acidic media. When a large excess of the ligand is present (Fig. 4), species containing more than one ligand per metal ion are favored and hydrolysis processes become noticeable only at higher pH values.

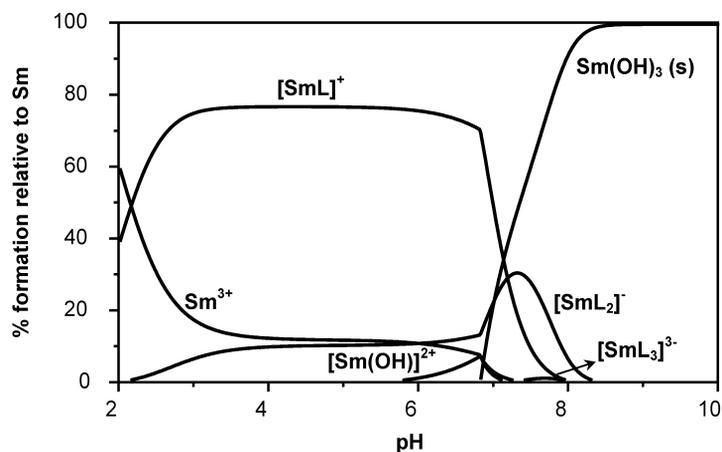


Fig. 3 Species distribution diagram for Sm-oda system at 25.0 °C, 0.50 M Me_4NCl . $[\text{Sm}] = [\text{oda}] = 1 \text{ mM}$. Protonation and complex formation constants were taken from [13] and samarium hydrolysis constant from [32]. Solubility constant product of $\text{Sm}(\text{OH})_3(\text{s})$ (taken from [32]) was also included in the calculation.

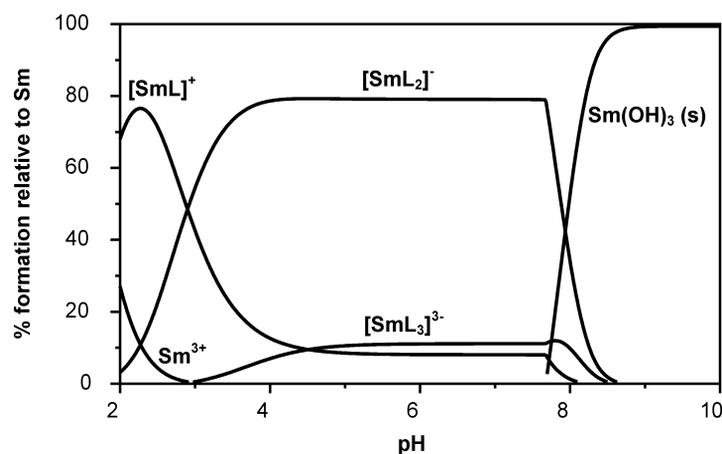


Fig. 4 Species distribution diagram for Sm-oda system at 25.0 °C, 0.50 M Me_4NCl . $[\text{Sm}] = 1 \text{ mM}$, $[\text{oda}] = 3 \text{ mM}$. Protonation and complex formation constants were taken from [13] and samarium hydrolysis constant from [32]. Solubility constant product of $\text{Sm}(\text{OH})_3(\text{s})$ (taken from [32]) was also included in the calculation.

For the ida ligand, formation of the species $[\text{Ln}(\text{L})]^+$, $[\text{Ln}(\text{L})_2]^-$, and $[\text{Ln}(\text{L})_3]^{3-}$ analogously to those present in Ln-oda systems was detected (Table 3). The species $[\text{Ln}(\text{L})_3]^{3-}$ only exists in a very narrow pH range before $\text{Ln}(\text{OH})_3$ precipitation takes place. For this reason, the overall formation constant exhibits a larger uncertainty and the value should be taken as an approximation. Species distribution diagrams are different for oda and ida ligands especially in acidic media due to the more basic character of the latter (Fig. 5). In fact, the higher affinity for H^+ of ida relative to oda accounts for the fact that Sm remains free in acidic media even though the stability constants of Sm-oda and Sm-ida complexes are similar. The ida ligand exhibits a stronger affinity than oda toward the Ln ions having the same denticity (Tables 2 and 3). This is coincident with the higher basicity of ida compared to oda.

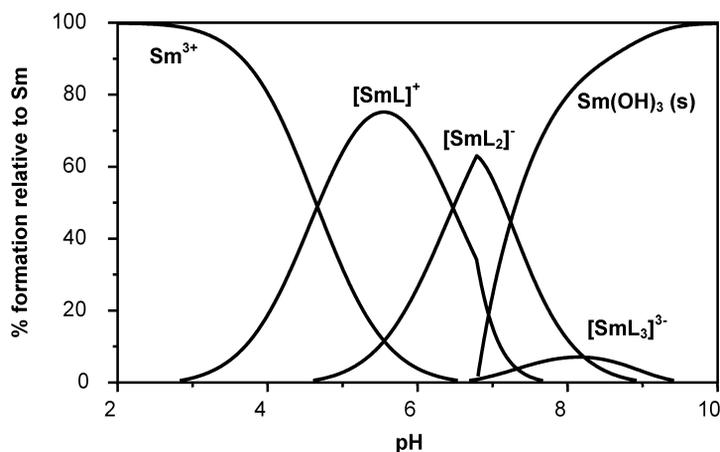


Fig. 5 Species distribution diagram for Sm-ida system at 25.0 °C, 0.50 M Me_4NCl . $[\text{Sm}] = 20 \text{ mM}$, $[\text{ida}] = 60 \text{ mM}$. Hydrolysis constant and solubility constant product of $\text{Sm}(\text{OH})_3(\text{s})$ (taken from [32]) were also included in the calculation.

Thermodynamic stability of 3d metal ions complexes with oda or ida

The ligand oda in the presence of bivalent and trivalent 3d cations also forms stable species (Table 2). This fact is also verified with ions like VO^{2+} and Al^{3+} . In particular, 1:1 species are always present in the systems. For most 2+ cations, $[\text{ML}]$ species are predominant. Only in the cases of VO^{2+} and Fe^{3+} cations, species containing 1:2 molar ratio (metal to ligand) are important in the speciation.

The overall formation constants of the species containing ida are depicted in Table 3. The predominance of 1:1 species is again notorious. The complexes with ida are also more stable than the oda analogs, due to the presence of an amino group. This fact can be verified by comparison of the $\log \beta_{110}$ values. The enhancement of stability is much more pronounced for the 3d metal ions than for the Ln ions, due to the harder character of the latter.

Thermodynamic stability of the polynuclear complexes

It would be very interesting to know if the polynuclear species formed by these two ligands with Ln ions and 3d transition-metal ions can also exist in solution. These studies have hitherto been very scarce. $\text{Ln}^{\text{III}}\text{-M}^{\text{II}}\text{-oda}$ ($\text{M} = \text{Cu}, \text{Mn}, \text{Ni}, \text{Fe}, \text{Co}, \text{Zn}, \text{Cd}, \text{and } \text{VO}^{2+}$) for $\text{Ln} = \text{La}$ and Sm , have been studied in aqueous solution, at 25.0 °C, and $I = 0.50 \text{ M Me}_4\text{NCl}$. In addition, a few systems containing M^{III} cations ($\text{M} = \text{Fe}, \text{Al}$) instead of M^{II} were also studied [13,18]. Our present results for $\text{Ce}^{\text{III}}\text{-M-oda}$ systems and the previously reported ones are depicted in Table 4.

Heterobimetallic species are found, if a Ln ion, oda, and a second metal ion are mixed in solution. Taking Sm^{3+} as an example, $[\text{Sm}_2\text{M}_3(\text{oda})_6(\text{OH})_3]^{3-}$ is present in many systems containing M^{2+} cations and represents the predominant species in solution (Fig. 6) at pH values near neutrality. It can be thought of as derived from the neutral less soluble species $[\text{Sm}_2\text{M}_3(\text{oda})_6(\text{H}_2\text{O})_6]$, isolated in the solid state. Hydroxide groups in the hydroxylated species are probably coordinated to M, taking into account the presence of coordinated water molecules in the crystal structure. Changing Cu by another $3d$ metal ion does not change the speciation dramatically (Fig. 6b). Trivalent cations, Fe^{3+} and Al^{3+} , like most $2+$ cations, predominate as 2:3:6 species, but in this case with a higher degree of deprotonation (Fig. 6c). Similar results were obtained for the other Ln ions: the same 2:3:6 stoichiometry was detected. In the case of La and Ce, although not Sm, the neutral species $[\text{Ln}_2\text{M}_3(\text{oda})_6]$ was also detected in solution for many systems (Fig. 6d).

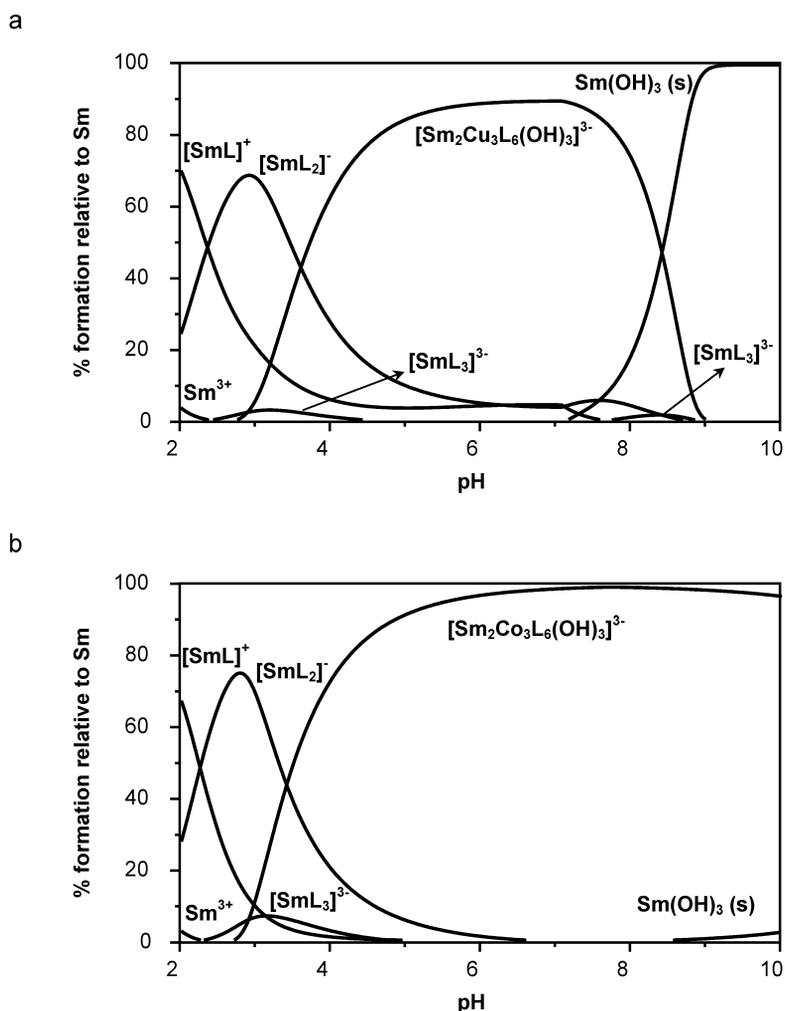


Fig. 6 Species distribution diagram of Ln-M-oda systems. Hydrolysis constants [18,32] and solubility constant products of $\text{Ln}(\text{OH})_3(\text{s})$ [32,35] were also included in the calculation. Conditions: 25.0 °C, $I = 0.50 \text{ M Me}_4\text{NCl}$, $[\text{Ln}^{3+}] = 10 \text{ mM}$, $[\text{M}] = 15 \text{ mM}$, $[\text{oda}] = 30 \text{ mM}$. (a) Ln = Sm, M = Cu^{II}, (b) Ln = Sm, M = Co^{II}, (c) Ln = Sm, M = Fe^{III}, (d) Ln = La, M = Co^{II}.

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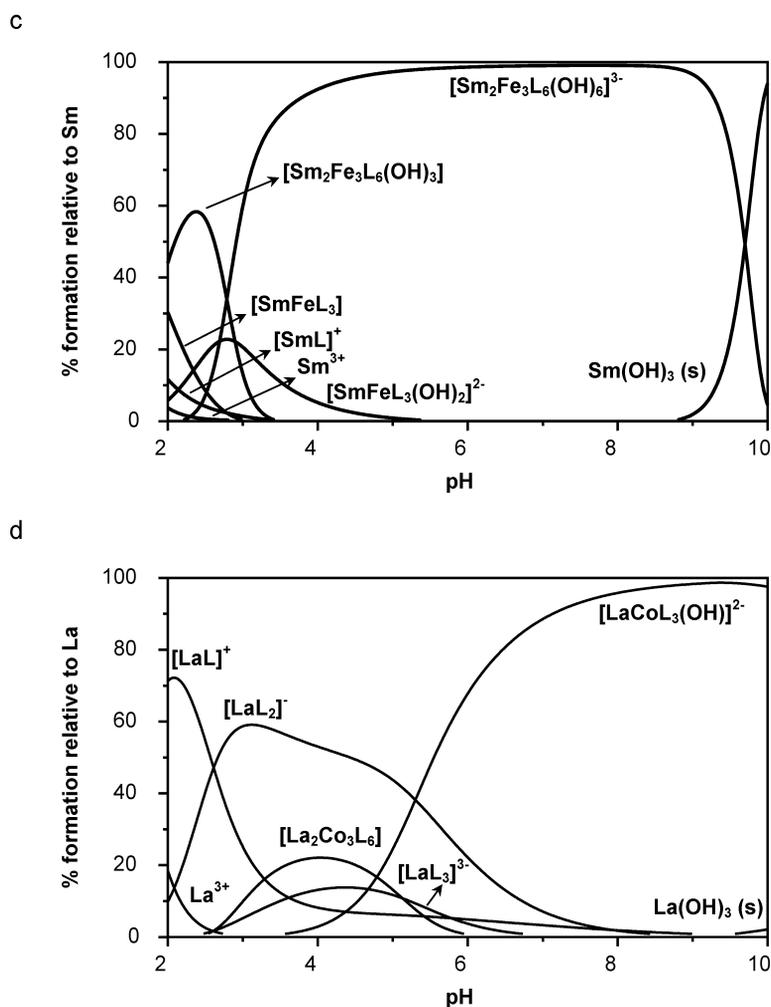


Fig. 5 (Continued).

The formation of polynuclear species with ida as bridging ligand is also verified in aqueous solution (Table 5), in particular those with formula $[\text{Sm}_2\text{M}_3(\text{ida})_6]$. The presence of an amino group in the ida ligand makes the species with $3d$ metal ions more stable (compared to oda, as discussed above), preventing to some extent the formation of polynuclear complexes. However, the polynuclear species are stable enough to be present in solution. In particular, the speciation in Cu-containing systems (Fig. 7a) still shows the predominance of $[\text{Sm}_2\text{Cu}_3(\text{ida})_6]$ near neutral pH values. If another metal ion instead of Cu is added to the Sm-ida system, polynuclear species are still detected but in lower percentage, due to the higher stability of M-ida complexes relative to the polynuclear Sm-ida-M (Fig. 7b). Above pH value of 6, the Ln ion is precipitated as $\text{Sm}(\text{OH})_3$ (Fig. 7b) because the ligand is coordinated to the $3d$ metal ion (Fig. 8).

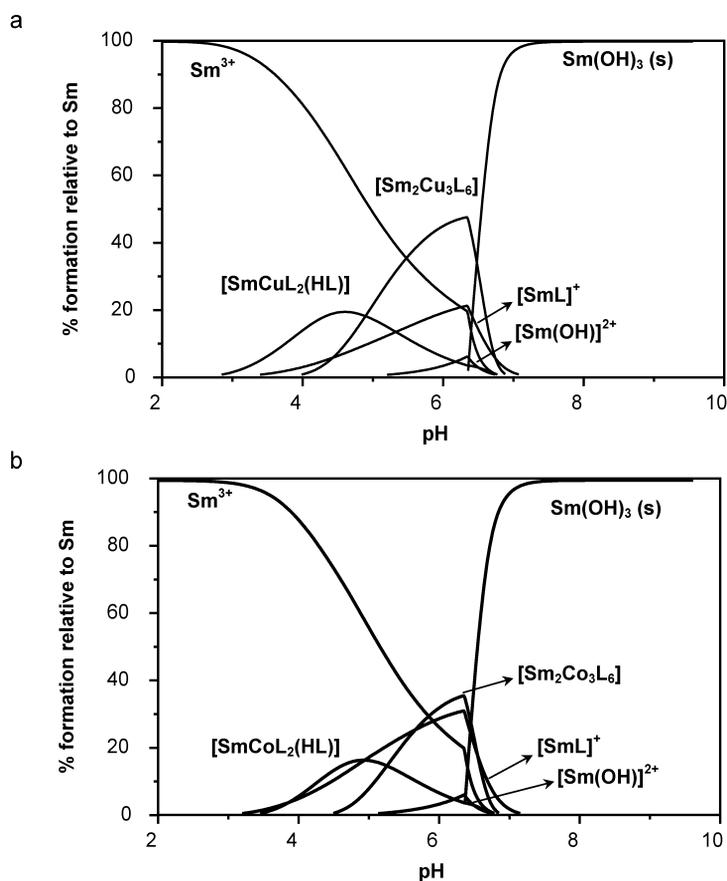


Fig. 7 Species distribution diagram of Sm-M-ida systems. Hydrolysis constant and solubility constant product of $\text{Sm}(\text{OH})_3(\text{s})$ [32] were also included in the calculation. Conditions: $25.0\text{ }^\circ\text{C}$, $I = 0.50\text{ M Me}_4\text{NCl}$, $[\text{Sm}^{3+}] = 10\text{ mM}$, $[\text{M}^{2+}] = 15\text{ mM}$, $[\text{ida}] = 30\text{ mM}$. (a) $M = \text{Cu}$, (b) $M = \text{Co}$.

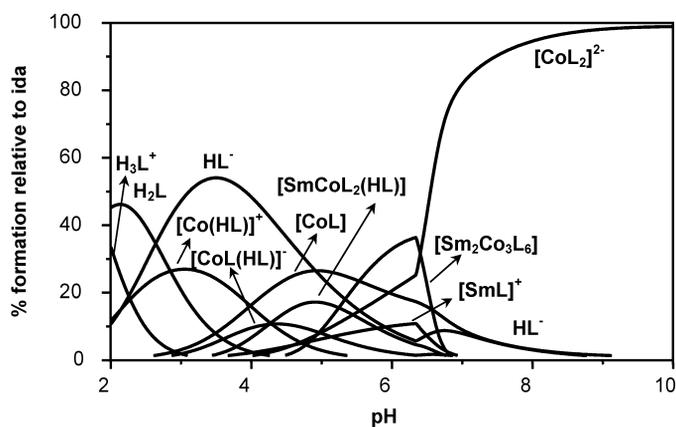


Fig. 8 Species distribution diagram of Sm-Co-ida systems. Hydrolysis constant and solubility constant product of $\text{Sm}(\text{OH})_3(\text{s})$ [32] were also included in the calculation. Conditions: $25.0\text{ }^\circ\text{C}$, $I = 0.50\text{ M Me}_4\text{NCl}$, $[\text{Sm}^{3+}] = 10\text{ mM}$, $[\text{Co}^{2+}] = 15\text{ mM}$, $[\text{ida}] = 30\text{ mM}$.

CONCLUDING REMARKS

Some general conclusions on the formation of the polynuclear species can be stressed, regarding the possibility to assay the complexes as homogeneous catalysts:

- Oda and ida ligands proved to bridge Ln^{III} ions and different divalent cations both in solution and in the solid state.
- Ln:M:oda 2:3:6 stoichiometry predominates in solution at pH values near neutrality.
- The chemical speciation is not markedly influenced by the Ln ion.
- M^{III} metal ions form more stable and more deprotonated species.
- The presence of an amino group in the ida bridging ligand prevents to some extent the predominance of polynuclear complexes.

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