DOI: 10.1002/masy.201150610

Modulation of the Physicochemical Properties of Heteropolynuclear Assemblies Containing Lanthanide Ions and 2,2′-oxydiacetate

Carlos Kremer,[*1] Julia Torres,[1] Florencia Peluffo,[1] Valentina Pintos,[1] Leopoldo Suescun,[2] Ricardo Faccio,[2] Alvaro W. Mombrú,[2] Sixto Domínguez[3]*

Summary: This work focuses on the polynuclear complexes formed by a lanthanide ion (Ln), a bivalent cation (M) and oxydiacetate (oda) as bridging ligand, with general formula $[Ln_2M_3(oda)_6(H_2O)_6] \cdot xH_2O$. The complexes can adopt more than one polymorphic structure, being the hexagonal (P6/mcc) and cubic (Fd3c) the most noticeable, as determined by x-ray powder diffraction. The influence of Ln and M on the solid-state structure is discussed. In addition, potentiometric studies are performed to support the existence of polynuclear species in solution.

Keywords: chemical speciation; inorganic materials; lanthanide complexes; self-assembly; x-ray powder diffraction

Introduction

The science of open-framework coordination polymers made from metal ions connected by bridging organic ligands has become a challenging issue for chemists, physicists and nanotechnologists over the last ten years.[1,2] The important applications of these supramolecular materials in the areas of ion-exchange, separation processes, catalysis and gas storage devices explain the rapid expansion of the research in this field.[3–5]

The first approach was the synthesis of homopolynuclear coordination compounds, containing a single metal ion, usually a 3d ion. Many examples of such compounds and their applications can be found in the literature.[6–8] The need for new materials with different solid state-properties encouraged the design of more sophisticated structures. Then, the design of heteropolynuclear complexes built with two or more metal ions opened new perspectives in this field. The combination of different coordination geometries in the same material produces compounds in which the structure and the properties can be modulated. We are interested in the design, preparation and characterization of polynuclear complexes containing a lanthanide ion (Ln(III)) and a bivalent metal ion (M(II)). The inclusion of a rare earth ion in the metal-organic frameworks gives further attraction because of the more varied coordination chemistry of the f-block elements.[9,10]

Among the potential bridges, the polycarboxylic acid H_2oda (2,2′-oxydiacetic acid, Figure 1) is able to produce an interesting set of polynuclear complexes. In 1997, it was reported that a mixture of Ln(III), Cu(II) and oda in aqueous solution produces the self-assembling of a neutral polynuclear complex with general formula

---

[1] Cátedra de Química Inorgánica, Departamento Estrella Campos, Facultad de Química, UdelaR, CC1157, Montevideo, Uruguay & Centro Interdisciplinario en Nanotecnología y Química y Física de Materiales, Espacios Interdisciplinarios, UdelaR
E-mail: ckremer@fq.edu.uy

[2] Laboratorio de Cristalografía, Estado Sólido y Materiales (Cryssmat-Lab), DETEMA, Facultad de Química, UdelaR, Montevideo, Uruguay & Centro Interdisciplinario en Nanotecnología y Química y Física de Materiales, Espacios Interdisciplinarios, UdelaR

[3] Departamento de Química Inorgánica, Universidad de La Laguna, Tenerife, Islas Canarias, Spain

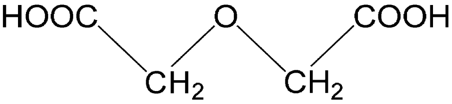

Figure 1.
2,2′-Oxydiacetic acid (H_2oda).

$[Ln_2Cu_3(oda)_6(H_2O)_6] \cdot xH_2O$.[11] The structure (hexagonal crystal system, space group P6/mcc) is made by $[Ln(oda)_3]$ building blocks, assembled by the presence of Cu(II) ions which connect the blocks in a supramolecular structure. The Ln metal ion is nine coordinated, being surrounded by nine oxygen atoms from three oda ligands. Copper atoms are six coordinated, being surrounded by six oxygen atoms, four from $[Ln(oda)_3]$ units, and two from water molecules (Figure 2a). The most interesting feature in the structures is the formation of a network containing large hexagonal channels (Figure 3a). The channels contain crystallization water molecules. Isostructural complexes were also found for other M(II) ions, like in $[La_2Co_3(oda)_6(H_2O)_6] \cdot xH_2O$.[12] The structures and properties of these complexes were previously reviewed.[13]

In 2007, a different self-assembling was obtained under similar synthetic conditions.[14] The mixture of Gd(III), Mn(II) and oda in aqueous solution produces a solid with the same stoichiometry $[Gd_2Mn_3(oda)_6(H_2O)_6] \cdot xH_2O$, but the solid-state symmetry is different (cubic crystal system, space group Fd3c). The $[Gd(oda)_3]$ units are present, but now there are inequivalent Mn ions in the structure. Two out of three are connected to Gd(III) through a carboxylate bridge (Figure 2b), and the third one remains as hexaaquo complex, filling the voids left by and neutralizing the $[Gd_2Mn_2(oda)_6]^{2-}$ anionic network in the solid state. The complex is then better described as $[\{Mn(H_2O)_6\}\{MnGd(oda)_3\}_2] \cdot xH_2O$. The structure is now cubic, very compact, without free space or channels (Figure 3b).

The change of structure produces different properties. The hexagonal phases exhibit H_2 uptake (up to 1.2 wt % at 77 K) after removing of the crystallization water molecules,[15] and at low temperatures, an antiferromagnetic coupling M(II)-M(II) is detected.[16,17] On the other hand, the more compact cubic phases do not show hydrogen uptake and at low temperatures the magnetic interactions Ln(III)-M(II) are ferromagnetic.[14]

Another important point in these polynuclear complexes is that they exist in aqueous solution. The potentiometric studies show that in many mixed-ion systems, the polynuclear species $[Ln_2M_3(oda)_6(OH)_n]^{n-}$ are predominant at pH values near neutrality.[18]

With this in mind, and following our previous works, we expanded the solution studies for the systems containing oda, a bivalent M(II) ion and Yb(III) or Gd(III). In addition, the formation of the different

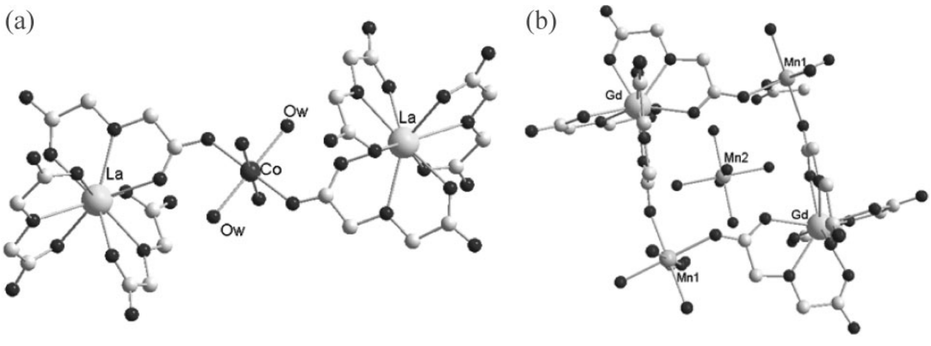

Figure 2.
Comparative bridged structures of $[La_2Co_3(oda)_6(H_2O)_6] \cdot xH_2O$ (a), and $[Gd_2Mn_3(oda)_6(H_2O)_6] \cdot xH_2O$ (b).

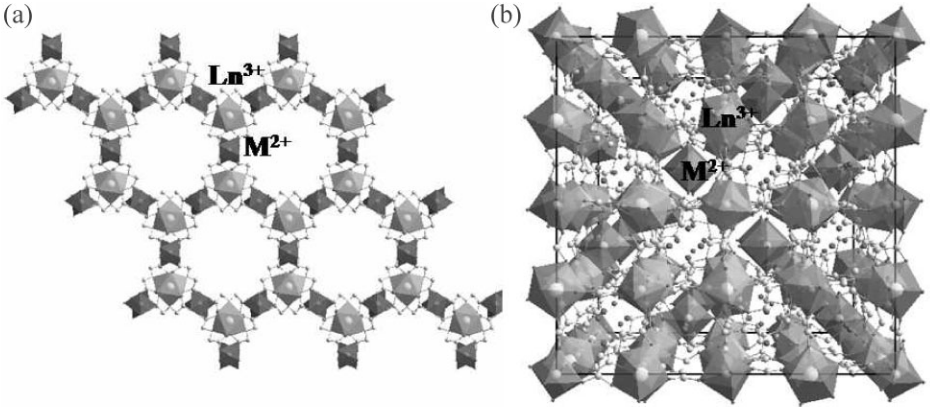

Figure 3.
Comparative packing of hexagonal (a, $[La_2Co_3(oda)_6(H_2O)_6] \cdot xH_2O$) and cubic (b, $[Gd_2Mn_3(oda)_6(H_2O)_6] \cdot xH_2O$) structures in $[Ln_2M_3(oda)_6(H_2O)_6] \cdot xH_2O$ complexes.

solid state structures for many heterobimetallic solids is studied by x-ray powder diffraction.

Experimental Part

Potentiometric Titrations

Solutions of the metal ions were standardized according to standard techniques.[19–21] 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 $Me_4N(OH)$ in 0.50 M Me_4NCl) was prepared by dissolving $Me_4N(OH) \cdot 5H_2O$ (Fluka), and standardized with potassium biphthalate. The hydrolysis constant of Yb^{3+} and Gd^{3+}, and the formation constants of Ln^{3+}–oda species were measured in the same conditions, by potentiometry. The protonation constants of the ligand oda, and the formation constants of M^{2+}–oda systems were taken from our previous reports.

In a typical procedure, Ln^{3+}-oda systems were analyzed through three potentiometric titrations (*ca.*150 experimental points each), at concentrations ranging from 3 to 15 mM, and Ln^{3+}:oda molar ratios ranging from 1:1 to 1:3. Then, the formation of the mixed species was tested by at least three other potentiometric titrations with Ln:M:oda molar ratios between 1:1:1 and 2:3:6, and different total concentrations of the components.

In all cases, the solutions were poured 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 $Me_4N(OH)$ solution (carried out with the help of 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 Ag/AgCl reference electrode. The experimental data were collected automatically as previously described.[22] 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. Pre-saturated 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-strong base titration using the GLEE program.[23] Data were analyzed using the HYPERQUAD program,[24] and species distribution diagrams were produced using the HySS program.[25] 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.

Synthesis of the Complexes

The complexes $[Ln_2M_3(oda)_6(H_2O)_6] \cdot xH_2O$ were obtained following the procedure previously reported.[12,17] The strategy is based in the mixture of stoichiometric amounts of LnX_3 (Ln = La, Ce, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb; X = Cl, NO_3), MX_2 (M = Mg, Ca, Mn, Co, Ni; X = Cl, CH_3COO, NO_3) and H_2oda in aqueous solution. The pH was adjusted to pH 6–7 with ammonium hydroxide, and the solution was allowed to evaporate slowly at room temperature. After 3–15 days, a polycrystalline solid was obtained. The purity was checked by elemental analysis (Carlo Erba EA 1108 instrument), IR spectra (Bomen MB FT-IR spectrophotometer) and thermal analysis (Shimadzu TGA-50 instrument with a TA 501 interface, using a platinum cell and nitrogen atmosphere). For the novel compounds, the analytical data are presented in Table 1.

X-ray Powder Diffraction

X-ray powder diffraction data were collected for all the polycrystalline solids obtained as previously described using a Rigaku ULTIMA IV, 285 mm radius, powder diffractometer. Cu*Kα* radiation (λ = 1.5418 Å) monochromatized with a diffracted beam bent germanium crystal was used to collect data over the 3–100 deg 2θ range in steps of 0.02 deg using a scintillation detector. Fixed slits 1/3 deg were used for data collection to prevent beam spillage outside the 2 cm long sample (along the beampath) at low angles. Peak positions were extracted from the difractogram using the program POWDERX[26] and peak indexing and unit cell determination was performed with DICVOL04[27] to determine the unit cell and space group symmetry of the solid.

Results and Discussion

Tables 2 and 3 compile the stability data at 25.0°, $I = 0.50$ M NMe_4Cl, for the systems under study, including those obtained in this work and those previously reported. The full description of these systems includes the Ln(III) hydrolysis, the protonation of the ligand, the formation of M(II)-oda and Ln(III)-oda species and finally, the polynuclear species.

The comparative analysis of stability constants in Table 3, reveals that polynuclear species with 2:3:6 molar ratio (Ln:M:oda) can be detected in solution,

Table 1.
Elemental analysis and water content of the novel complexes obtained.

Compound	Anal. Calcd. (%)			Found (%)		
	C	H	water	C	H	water
$[Ce_2Co_3(oda)_6(H_2O)_6] \cdot 12H_2O$	18.3	3.8	20.6	17.8	3.9	20.9
$[Gd_2Ca_3(oda)_6(H_2O)_6] \cdot 4H_2O$	20.2	3.1	12.8	21.5	3.5	12.6
$[Gd_2Co_3(oda)_6(H_2O)_6] \cdot 12H_2O$	17.9	3.8	20.1	17.9	3.7	20.1
$[Gd_2Ni_3(oda)_6(H_2O)_6] \cdot 12H_2O$	17.9	3.8	20.1	18.0	4.0	19.5
$[Dy_2Ca_3(oda)_6(H_2O)_6] \cdot 4H_2O$	20.3	3.1	12.7	20.4	3.3	13.1
$[Ho_2Mg_3(oda)_6(H_2O)_6] \cdot 4H_2O$	20.2	3.1	12.6	20.7	4.1	12.0
$[Ho_2Ca_3(oda)_6(H_2O)_6] \cdot 4H_2O$	20.2	3.1	12.7	19.7	3.4	12.5
$[Er_2Mg_3(oda)_6(H_2O)_6] \cdot 4H_2O$	20.2	3.1	12.7	18.6	3.5	12.5
$[Er_2Ca_3(oda)_6(H_2O)_6] \cdot 4H_2O$	20.2	3.1	12.6	20.4	3.4	12.2
$[Yb_2Mg_3(oda)_6(H_2O)_6] \cdot 4H_2O$	20.7	3.2	12.9	21.8	3.4	12.0
$[Yb_2Ca_3(oda)_6(H_2O)_6] \cdot 4H_2O$	20.0	3.1	12.5	21.2	3.4	12.3
$[Yb_2Mn_3(oda)_6(H_2O)_6] \cdot 4H_2O$	19.4	3.0	12.1	20.9	3.1	11.2
$[Yb_2Co_3(oda)_6(H_2O)_6] \cdot 4H_2O$	19.3	3.0	12.0	20.1	3.1	12.3

Table 2.
Hydrolysis of Ln cations and overall formation constants for Ln-oda complexes at 25.0 °C, $I = 0.50$ M Me_4NCl.

	Ln hydrolysis		Ln-oda complexes			
	$Ln^{3+} + H_2O \rightarrow [Ln(OH)]^{2+} + H^+$	σ	β_{110}	β_{120}	β_{130}	σ
Yb(III)	−7.22(3)	1.0	3.90(8)	7.93(6)	10.7(1)	0.7
Gd(III)	−7.816(9)	1.1	5.92(3)	10.91(4)	13.73(5)	0.1

Table 3.
Overall formation constants for Ln-M-oda complexes, 25.0 °C, $I = 0.50$ M Me_4NCl. The data for Ce, La, and Sm were taken from J. Torres et al.[18] β_{pqrs} corresponds to the equilibria: $pLn^{3+} + qM^{2+} + rL^{2-} + sH^+ \leftrightarrow [Ln_pM_qL_rH_s]^{(2r\text{-}3p\text{-}2q\text{-}s)-}$ $(s > 0)$; $pLn^{3+} + qM^{2+} + rL^{2-} + sH_2O \leftrightarrow [Ln_pM_qL_r(OH)_s]^{(2r+s\text{-}3p\text{-}2q)-} + sH^+$ $(s < 0)$. L denotes fully deprotonated oda.

Ln	M	Equilibrium formation constant (log β_{pqrs})					σ
		$[Ln_2M_3L_6]$	$[Ln_2M_3L_6(OH)_3]^{3-}$	$[LnML_3]^-$	$[LnML_3(OH)]^{2-}$	$[LnML_3H_2]^+$	
La	Mn^{2+}	30.32(4)	18.40(8)				
	Fe^{2+}		17.11(4)	12.54(3)			
	Co^{2+}	29.6(2)			7.72(8)		
	Ni^{2+}	30.49(5)			8.31(5)		
	Cu^{2+}	32.52(6)			11.19(2)		
	Zn^{2+}	31.6(1)			9.78(3)		
	Cd^{2+}	30.5(1)			8.92(4)		
Ce	Mg^{2+}				10.49 (3)		
	Ca^{2+}				11.91(2)		
	Mn^{2+}			12.18(7)	7.45(6)		
	Fe^{2+}		16.75(7)	13.04(2)			
	Co^{2+}	30.04(6)					
	Ni^{2+}			13.63(2)		19.49(2)	
	Cu^{2+}			13.05(4)		18.09(8)	
	Zn^{2+}	31.81(8)			10.73(3)		
	Cd^{2+}				7.79(4)		
Sm	Mn^{2+}		24.6(1)		11.76(3)		
	Fe^{2+}		24.1(1)		12.11(3)		
	Co^{2+}		23.46(5)				
	Ni^{2+}		22.80(6)				
	Cu^{2+}		24.60(7)				
	Zn^{2+}		24.35(5)				
	Cd^{2+}		22.88(7)				
Gd	Mg^{2+}			12.5(1)	9.87(2)		1.5
	Ca^{2+}		20.14(9)				1.3
	Fe^{2+}	30.68(9)			8.10(3)		1.1
	Co^{2+}		22.08(4)				1.4
	Ni^{2+}		23.47(6)				1.9
	Mn^{2+}	32.49(5)	22.84(3)		10.78(2)		0.6
	Cu^{2+}				10.94(3)		0.7
	Zn^{2+}		23.73(2)				1.0
	Cd^{2+}		21.85(4)				1.9
Yb	Mg^{2+}	34.78(2)	17.25(9)				0.4
	Ca^{2+}				11.55(9)		1.6
	Fe^{2+}	35.83(7)		15.98(2)	11.78(2)		0.3
	Co^{2+}	34.64(4)					0.2
	Ni^{2+}	35.19(6)					1.0
	Mn^{2+}	34.38(4)	19.33(9)				0.3
	Cu^{2+}			16.46(3)			0.7
	Zn^{2+}		24.31(9)	15.60(5)			0.9
	Cd^{2+}				9.13(4)		0.2

regardless Ln and M. The species appear as neutral complexes $[Ln_2M_3(oda)_6]$ or in a deprotonated form $[Ln_2M_3(oda)_6(OH)_3]^{3-}$, being OH groups originated in the deprotonation of coordinated water molecules. It should be mentioned that other models (excluding the polymeric species) were tried, but they did not fit properly with the experimental data. This fact, together with the isolation of the polynuclear species at solid state (see below) support the existence of these species in solution.

The isolation of the polynuclear complexes does not depend only on the existence of these species in solution. They should, at least, be predominant in certain pH range. This can be visualized through a species distribution diagram. Figure 4 shows two diagrams for the systems Gd-Mn-oda and Yb-Ni-oda under similar conditions. Over pH 5, $[Gd_2Mn_3(oda)_6(OH)_3]^{3-}$ is the dominant Gd species, and the isolation of the polynuclear compound would be a probable task. However, the Yb–Ni–oda system exhibits the predominance of mononuclear species. The complex $[Yb_2Ni_3(oda)_6]$ only represents 13% of the total amount of Yb between pH 4 and 8.

We have also begun a systematic study of the solid phases that can be obtained in the mixed ion systems. The solids obtained by slow evaporation of aqueous solutions containing stoichiometric amounts of Ln(III), M(II) and oda at pH 7, were analyzed in composition (C, N and H percentages) and water content (Table 1). The IR spectra of the complexes follow a common pattern with the characteristic peaks of the oda ligand at 1605, 1439, and $1124\,cm^{-1}$. The TGA diagrams show a weight loss corresponding to the water molecules in the range 50 to 120 °C. Decomposition of the solids became evident over 200 °C.

The solids were also studied by x-ray powder diffraction. This method provides the unambiguous differentiation of the hexagonal and cubic phases of the polynuclear complexes. As an example, the powder diffractograms of $[Gd_2Co_3(oda)_6(H_2O)_6] \cdot xH_2O$ (Hexagonal, P6/mcc, a = 14.807(6) Å, c = 15.676(11) Å, V = 2976.71 Å^3) and

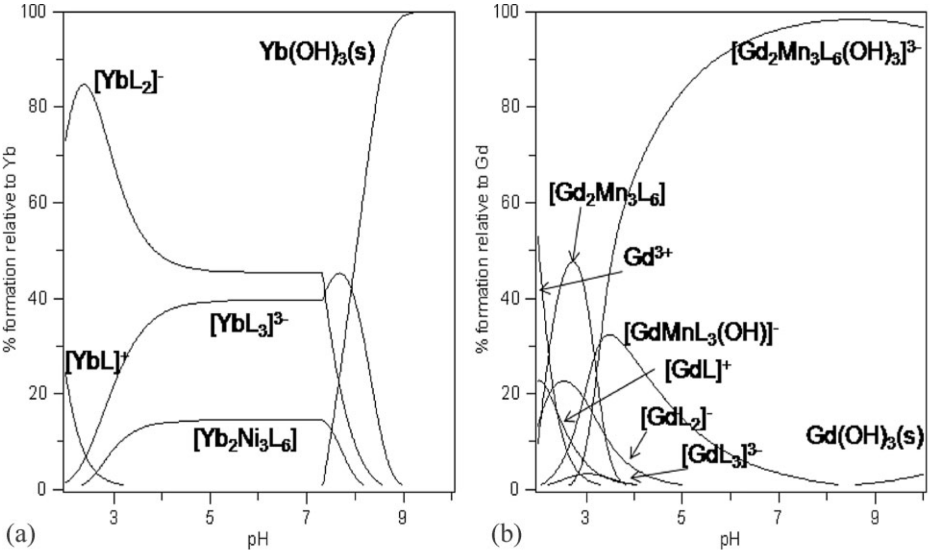

Figure 4.
Species distribution diagrams of Yb-Ni-oda (a) and Gd-Mn-oda (b) systems. Hydrolysis constants and solubility constant products of $Ln(OH)_3(s)$ [28,29] were also included in the calculations. Conditions: 25.0 °C, $I = 0.50$ M Me_4NCl, $[Ln^{3+}] = 10$ mM, $[M^{2+}] = 15$ mM, $[oda] = 30$ mM.

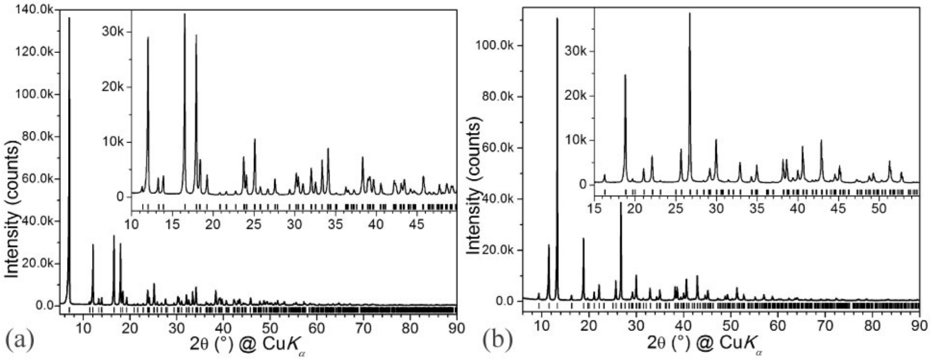

Figure 5.
Indexed x-ray powder diffractograms for $[Gd_2Co_3(oda)_6(H_2O)_6]\cdot xH_2O$ (a) and $[\{Ca(H_2O)_6\}\{CaGd(oda)_3\}_2]\cdot xH_2O$. Vertical lines below the pattern correspond to peak position. The insets show the detail of the peaks at intermediate values of 2θ.

$[\{Ca(H_2O)_6\}\{CaGd(oda)_3\}_2]\cdot xH_2O$ (Cubic, Fd3c, a = 26.6408(11) Å, V = 18907.84 Å^3) are shown in Figure 5 a and b respectively.

The solids, according to the composition, can be divided in two groups. Some of them, fit the composition $[Ln_2M_3(oda)_6(H_2O)_6]\cdot xH_2O$, being the structure either hexagonal or cubic. The second group corresponds to monomers $(NH_4)[M(H_2O)_6][Ln(oda)_3]\cdot xH_2O$. The existence of this group of complexes is consistent with the potentiometric results which foresee some unstable mixed-ion compounds. In addition, some solids appear as a mixture of phases different from the hexagonal, cubic or monomeric ones. This information is summarized in Figure 6, which includes the solids studied in this work as well as those previously reported.

The comparative analysis of the solid state structures, shows that the hexagonal (channelled) structures seem to be favoured for large lanthanide ions and bivalent cations with a marked tendency towards 4 + 2 distorted octahedral coordination (like Cu, Ni and sometimes Co),

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Y	Er	Yb
Mg	N	N			M					C		C	C
Ca	M			M	C		C		C	C		C	C
Mn	N	N			C		C$^{a)}$						C
Co	H$^{a)}$	H			H/C$^{a)}$		H		N				C/N
Ni	H	N			H	H	H						N
Cu	H$^{a)}$	H$^{a)}$	H$^{a)}$	H$^{a)}$	H$^{a)}$	H$^{a)}$	H$^{a)}$	H$^{a)}$	H$^{a)}$	H$^{a)}$	H$^{a)}$	H$^{a)}$	H$^{a)}$
Zn					H$^{a)}$								

Figure 6.
Structural characteristics of the solids obtained from 3:2:6 (M:Ln:oda) solutions as described above. H: hexagonal structure; C: cubic structure; N: monomeric structure, M: phase mixture not including H, C or N phases. Empty cells correspond to untested compositions. $^{a)}$Structures studied by single crystal x-ray diffraction, and previously reported.[11,14,16,17,30–34]

while cubic (compact) structures are found for small lanthanides and isotropic M(II) cations. Cu(II) complexes are a particularly special case, in which the cation forces the hexagonal structures due to its anisotropy for all Ln cations. The hexagonal structure allows the presence of an elongated Cu(II) octahedron with two coordinated water molecules in the apical direction.

There are other parameters which could influence the preference for a given structure. For example, the more favorable hydration enthalpy of the M(II) ions (which could favor cubic structures), and the tendency to form hydrated ions with coordination numbers different than 6. They are expected to be important, but they are more difficult to evaluate.

Conclusion

The complexes of general composition $[Ln_2M_3(oda)_6] \cdot xH_2O$ present a very reach solid-state chemistry. Different architectures can be found depending on Ln and M, being the cubic and hexagonnal structures the most remarkable ones. The full analysis of the crystal structures, as well as the solid-sate transformation of one into the other, are now under way and will be published elsewhere.

[1] P. A. Wright, "*Microporous Framework Solids*", RSC Publishing, Cambridge 2008.

[2] D. Maspoch, D. Ruiz-Molina, J. Veciana, *Chem. Soc. Rev.* **2007**, *36*, 770.

[3] R. E. Morris, P. S. Wheatley, *Angew. Chem. Int. Ed.* **2008**, *47*, 4966.

[4] T. Uemura, N. Yanai, S. Kitagawa, *Chem. Soc. Rev.* **2009**, *38*, 1228.

[5] A. U. Czaja, N. Trukhan, U. Müller, *Chem. Soc. Rev.* **2009**, *38*, 1284.

[6] J. .J Perry, IV, J. A. Perman, M. J. Zaworotko, *Chem. Soc. Rev.* **2009**, *38*, 1400.

[7] S. Qiu, G. Zhu, *Coord. Chem. Rev.* **2009**, *253*, 2891.

[8] R. J. Kuppler, D. J. Timmons, Q. R. Fang, J. R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang, H. C. Zhou, *Coord. Chem. Rev.* **2009**, *253*, 3042.

[9] M. D. Allendorf, C. A. Brauer, R. K. Bhakta, R. J. T. Houk, *Chem. Soc. Rev.* **2009**, *38*, 1330.

[10] J. C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *4*, 1048.

[11] J. G. Mao, L. Song, X. Y. Huang, J. S. Huang, *Polyhedron* **1997**, *16*, 963.

[12] S. Domínguez, J. Torres, F. Peluffo, A. Mederos, J. González-Platas, J. Castiglioni, C. Kremer, *J. Mol. Struct.* **2007**, *829*, 57.

[13] C. Kremer, J. Torres, S. Domínguez, *J. Mol. Struct.* **2008**, *879*, 130.

[14] T. K. Prasad, M. V. Rajasekharan, J. P. Costes, *Angew. Chem. Int. Ed.* **2007**, *46*, 2851.

[15] Y. Wang, P. Cheng, J. Chen, D. Z. Liao, S. P. Yan, *Inorg. Chem.* **2007**, *46*, 4530.

[16] R. Baggio, M. T. Garland, Y. Moreno, O. Peña, M. Perec, E. Spodine, *J. Chem. Soc., Dalton Trans.* **2000**, 2061.

[17] J. Torres, F. Peluffo, S. Domínguez, A. Mederos, M. Arrieta, J. Castiglioni, F. Lloret, C. Kremer, *J. Mol. Struct.* **2006**, *825*, 60.

[18] J. Torres, C. Kremer, S. Domínguez, *Pure Appl. Chem.* **2008**, *80*, 1303.

[19] G. Schwarzenwach, H. Flaschka, "*Complexometric Titrations*", Methuen, London 1969.

[20] I. M. Kolthoff, E. B. Sandell, E. J. Meetran, S. Bruckenstein, "*Análisis Químico Cuantitativo*", Niger, Buenos Aires **1956**.

[21] R. B. Fischer, D. G. Peters, "*Análisis Químico Cuantitativo*", Interamericana, México 1970.

[22] J. Sanchiz, S. Domínguez, A. Mederos, F. Brito, J. M. Arrieta, *Inorg. Chem.* **1997**, *36*, 4108.

[23] P. Gans, B. O'Sullivan, *Talanta* **2000**, *51*, 33.

[24] P. Gans, A. Sabatini, A. Vacca, *Talanta* **1996**, *43*, 1739.

[25] L. Alderighi, P. Gans, A. Ienco, D. Peters, A. Sabatini, A. Vacca, *Coord. Chem. Rev.* **1999**, *184*, 311.

[26] C. Dong, *J. Appl. Cryst.* **1999**, *32*, 383.

[27] A. Boultif, D. Louer, *J. Appl. Cryst.* **2004**, *37*, 724–731.

[28] N. Akselrud, *Zh. Neorg. Khim.* **1960**, *5*, 1910.

[29] N. D. Ngo, K. Burkov, *Zh. Neorg. Khim.* **1974**, *19*, 1249.

[30] J. G. Mao, J. S. Huang, *Transition Met. Chem.* **1997**, *22*, 277.

[31] J. G. Mao, L. Song, J. S. Huang, *Chinese J. Struct. Chem. (Jiegou Huaxue)* **1997**, *16*, 228.

[32] B. Barja, R. Baggio, M. T. Garland, P. F. Aramendia, O. Peña, M. Perec, *Inorg. Chim. Acta* **2003**, *346*, 187.

[33] A. C. Rizzi, R. Calvo, R. Baggio, M. T. Garland, O. Peña, M. Perec, *Inorg. Chem.* **2002**, *41*, 5609.

[34] Q. D. Liu, J. R. LI, S. Gao, B. Q. Ma, F. H. Liao, Q. Z. Zhou, K. B. Yu, *Inorg. Chem. Commun.* **2001**, *4*, 301.