

# Gadolinium(III) and europium(III) L-glutamates: Synthesis and characterization

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## Abstract

Two lanthanide(III) complexes with L-glutamate ligands  $[\{\text{Ln}_2(\text{L-Glu})_2(\text{H}_2\text{O})_8\} \cdot 4(\text{ClO}_4) \cdot 2.5\text{H}_2\text{O}]_n$  (Ln = Gd (**1**), Eu (**2**)) have been prepared and characterized by single-crystal X-ray diffraction. The compounds are isomorphous with infinite cationic 2D layers stacked together by secondary bonds. The building blocks are slightly different non-centrosymmetric dinuclear units placed in alternating layers, the resulting structures thus containing four non-equivalent Ln metal sites. The dinuclear units contain a fourfold bridge, two in the  $\eta^1:\eta^1:\mu_2$  and two in the  $\eta^2:\eta^1:\mu_2$  modes, from two  $\alpha$ - and two  $\gamma$ -carboxylates of four different L-Glu residues, respectively.

*Keywords:* L-Glutamic acid; Gadolinium; Europium; X-ray structures; Spectroscopy

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## 1. Introduction

Ln/amino acid systems are of current interest because of the extensive use of lanthanide compounds as spectroscopic and structural metal probes in the study of active sites in metal enzymes [1–4] and in medicinal chemistry [5]. Recent studies on calcium and magnesium metalloproteins using the “quick cryosoaking” procedure [6–10] show that Gd(III) and Eu(III) can often bind to L-glutamate residues without changing their native structure. In addition, Gd(III) has been shown to partially support the catalytic activity of Mg(II) in ADPRase [11]. Most studies on Ln/amino acid model complexes are based on the chemical and photophysical properties of the Ln compounds, mainly

efficient emission in the UV to IR regions, NMR and EPR [9]. Definite structural interpretation, however, can only be given by X-ray diffraction, a technique generally limited to crystalline complexes. Although nearly 70 structures of Ln/amino acid complexes have been reported [12–14], only four of them are glutamates:  $[\{\text{Pr}_2(\text{Glu})_2(\text{ClO}_4)(\text{H}_2\text{O})_7\} \cdot 3(\text{ClO}_4) \cdot 4\text{H}_2\text{O}]_n$  [15],  $[\{\text{Sm}_2(\text{Glu})_2(\text{H}_2\text{O})_8\} \cdot 4(\text{ClO}_4) \cdot 3\text{H}_2\text{O}]_n$  [16],  $[\{\text{Dy}_2(\text{Glu})_2(\text{H}_2\text{O})_8\} \cdot 4(\text{ClO}_4) \cdot \text{H}_2\text{O}]_n$  and  $[\text{Ho}_2(\text{Glu})_2(\text{H}_2\text{O})_8] \cdot 4(\text{ClO}_4) \cdot \text{H}_2\text{O}]_n$  [17]. These four structures are built by infinite 2D planes with pairs of metal centers of nine-coordinate geometries linked by fourfold carboxylate bridges, two in the  $\eta^1:\eta^1:\mu_2$  and two in the  $\eta^2:\eta^1:\mu_2$  modes. The larger Pr cation crystallizes in  $P2_12_12_1$  with one perchlorate oxygen in the metal coordination core, whereas Sm, Dy and Ho crystallize in  $P2_1$ . Herein, we extend these studies to the gadolinium and europium L-glutamate systems:  $[\{\text{Ln}_2(\text{L-Glu})_2(\text{H}_2\text{O})_8\} \cdot 4(\text{ClO}_4) \cdot 2.5\text{H}_2\text{O}]_n$  (Ln = Gd (**1**), Eu (**2**)) which crystallize in  $P2_1$ . The availability of a

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series of isostructural organolanthanide frameworks may allow a comparative study of the roles of the individual lanthanides in the same host, as well as the development of materials with tunable properties via the replacement of the lanthanide cations.

## 2. Experimental

### 2.1. General

All starting materials were purchased from Aldrich and used without further purification. Elemental analyses (C, H, N) were performed on a Carlo Erba EA 1108 instrument. Infrared spectra were recorded on a Nicolet FT-IR 510 P spectrophotometer as KBr pellets or Nujol mulls in the range 4000–350  $\text{cm}^{-1}$ . Thermal analysis was performed on a Shimadzu DTG 50 thermal analyzer under air flow (40 L/min) at a heating rate of 5  $^{\circ}\text{C min}^{-1}$ . EPR spectra on polycrystalline samples were obtained at room temperature with a 9.4 GHz Bruker spectrometer using a Bruker rectangular cavity with 100 kHz field modulation. The luminescence emission spectra of the europium compound **2** were recorded on a PTI QuantaMaster QM-1 luminescence spectrometer at 298 and at 77 K.

### 2.2. Preparations

#### 2.2.1. [ $\{\text{Gd}_2(\text{L-Glu})_2(\text{H}_2\text{O})_8\} \cdot 4(\text{ClO}_4) \cdot 2.5\text{H}_2\text{O}\}_n$ (**1**)]

To a suspension of  $\text{Gd}_2\text{O}_3$  (0.36 mg, 1 mmol) in water (5 mL) was added 0.4 mL of concentrated  $\text{HClO}_4$  acid ( $\sim 70\%$ ) (0.60 mg, 6 mmol) under continuous stirring at

60  $^{\circ}\text{C}$ . After cooling to room temperature, L-glutamic acid (0.30 mg, 0.2 mmol) was dissolved under stirring and filtered. The clear solution was left standing in a stoppered flask for a year, whereupon colorless crystals of compound **1** were collected. Yield:  $\approx 40\%$ . *Anal.* Calc. for  $\text{C}_{10}\text{H}_{10}\text{Cl}_4\text{Gd}_2\text{O}_{34.5}$ : C, 10.30; H, 0.86; N, 2.40. Found: C, 10.20; H, 0.85; N, 2.38%. Main FT IR bands (KBr,  $\text{cm}^{-1}$ ): 1652 and 1624 vs.

$\delta_d(\text{NH}_3^+) + \nu_a(\text{CO}_2^-)$ , 1493 and 1483 m  $\delta_s(\text{NH}_3^+)$ , 1452 and 1427 s  $\nu_s(\text{CO}_2^-)$ , 1364 m, 1343 m, 1327 m, 1315 m, 1260 w, 1145 and 1089 vs  $\nu_a(\text{ClO}_4^-)$ , 993 m, 961 and 940 m  $\nu_s(\text{ClO}_4^-)$ , 850 m, 783 m, 726 m, 636 vs, 627 vs  $\rho(\text{CO}_2^-)$ , 560 m, 503 w.

#### 2.2.2. [ $\{\text{Eu}_2(\text{L-Glu})_2(\text{H}_2\text{O})_8\} \cdot 4(\text{ClO}_4) \cdot 2.5\text{H}_2\text{O}\}_n$ (**2**)]

Compound **2** was prepared in a fashion similar to that for **1** with  $\text{Eu}_2\text{O}_3$  instead of  $\text{Gd}_2\text{O}_3$  and crystals suitable for single crystal study were isolated after five months. *Anal.* Calc. for  $\text{C}_{10}\text{H}_{10}\text{Cl}_4\text{Eu}_2\text{O}_{34.5}$ : C, 10.15; H, 0.85; N, 2.37. Found: C, 10.05; H, 0.85; N, 2.35%. The IR spectrum is similar within  $\pm 5 \text{ cm}^{-1}$  to that described for **1** in the preceding paragraph.

*Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care.

### 2.3. X-ray crystallography

X-ray quality single crystals with a drop of their mother liquors were sealed in thin-walled glass capillaries and data were collected at room temperature (293(2) K) on a Bruker SMART CCD diffractometer, with graphite monochro-

Table 1  
Crystal and structure refinement data for **1** and **2**

Compound	Gd ( <b>1</b> )	Eu ( <b>2</b> )
Formula	$\text{C}_{10}\text{H}_{37}\text{Cl}_4\text{Gd}_2\text{N}_2\text{O}_{34.50}$	$\text{C}_{10}\text{H}_{37}\text{Cl}_4\text{Eu}_2\text{N}_2\text{O}_{34.50}$
MW	1193.72	1183.14
<i>a</i> (Å)	11.020(2)	11.0228(9)
<i>b</i> (Å)	16.616(3)	16.6244(13)
<i>c</i> (Å)	19.994(4)	20.0318(16)
$\alpha$ ( $^{\circ}$ )	90	90
$\beta$ ( $^{\circ}$ )	102.948(3)	102.8740(10)
$\gamma$ ( $^{\circ}$ )	90	90
<i>V</i> (Å <sup>3</sup> )	3568.0(12)	3578.5(5)
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.211	2.185
$\mu$ (mm <sup>-1</sup> )	4.104	3.891
Crystal dimensions (mm)	0.30 × 0.20 × 0.16	0.24 × 0.18 × 0.12
$\theta$ Range ( $^{\circ}$ )	1.90–27.52	1.61–28.02
Index range	$-10 \leq h \leq 14, -21 \leq k \leq 21, -25 \leq l \leq 25$	$-13 \leq h \leq 14, -21 \leq k \leq 20, -26 \leq l \leq 26$
Number of reflections: total, unique ( <i>R</i> <sub>int</sub> ), observed	20687, 13904 (0.0265), 12164	30174, 15100 (0.0373), 13049
Transmission range	0.5597 and 0.3724	0.6525 and 0.4553
<i>S</i>	1.012	1.012
<i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> <sup>a</sup> = 0.0394, <i>wR</i> <sub>2</sub> <sup>b</sup> = 0.0875	<i>R</i> <sub>1</sub> = 0.0440, <i>wR</i> <sub>2</sub> = 0.1032
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0470, <i>wR</i> <sub>2</sub> = 0.0907	<i>R</i> <sub>1</sub> = 0.0522, <i>wR</i> <sub>2</sub> = 0.1085
Maximum and minimum residual density $\Delta\rho$ (e Å <sup>-3</sup> )	1.891 and -1.152	1.408 and -1.343

Data in common: *T* = 293(2) K;  $\lambda$  = 0.71073 Å, crystal system = monoclinic, space group: *P*2<sub>1</sub>, *Z* = 4, absorption corrections type = semi-empirical from equivalents, parameters refined = 958.

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

mated Mo K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The solid colorless crystalline solids appear to be hygroscopic and slowly lose their shape in air. The structures were primarily solved by direct methods and completed by difference Fourier synthesis. Refinement of the model was performed by full-matrix least-squares techniques with anisotropic thermal factors for all non-H atoms. Theoretical models fixed the hydrogen atoms of the compounds. All calculations were performed using the program package SHEXL 97 [18]. Full use of the CCDC package was made using the CSD Data-

base [19,20]. Crystal and refinement data are shown in Table 1.

### 3. Results and discussion

Compounds **1** and **2** were isolated from concentrated aqueous solutions of gadolinium and europium perchlorate with L-glutamic acid (5:1 ratio) at pH 3. The reaction mixtures were left to stand capped at room temperature over long periods of time (a year for **1** and five months for **2**).

Table 2  
Selected bond lengths ( $\text{\AA}$ ) for **1** and **2**<sup>a</sup>

Ln-O	Gd-O (1)	Eu-O (2)	Ln-O	Gd-O (1)	Eu-O (2)
Ln(1 <sup>a</sup> )-O(4B)#1	2.398(5)	2.402(5)	Ln(1C)-O(1D)	2.410(5)	2.414(5)
Ln(1 <sup>a</sup> )-O(2WA)	2.406(6)	2.431(6)	Ln(1C)-O(2C)	2.414(6)	2.413(6)
Ln(1 <sup>a</sup> )-O(1B)	2.413(5)	2.428(5)	Ln(1C)-O(3WC)	2.428(6)	2.440(5)
Ln(1 <sup>a</sup> )-O(4WA)	2.417(6)	2.425(6)	Ln(1C)-O(4WC)	2.439(6)	2.440(7)
Ln(1 <sup>a</sup> )-O(3WA)	2.437(6)	2.446(5)	Ln(1C)-O(1WC)	2.465(5)	2.483(5)
Ln(1 <sup>a</sup> )-O(2 <sup>a</sup> )	2.444(6)	2.444(6)	Ln(1C)-O(2WC)	2.487(6)	2.494(6)
Ln(1 <sup>a</sup> )-O(4 <sup>a</sup> )#2	2.473(5)	2.490(5)	Ln(1C)-O(4C)#4	2.488(5)	2.502(5)
Ln(1 <sup>a</sup> )-O(1WA)	2.485(5)	2.504(5)	Ln(1C)-O(3C)#4	2.528(6)	2.532(6)
Ln(1 <sup>a</sup> )-O(3 <sup>a</sup> )#2	2.491(6)	2.498(6)			
Ln(1B)-O(1 <sup>a</sup> )	2.339(5)	2.340(5)	Ln(1D)-O(1C)	2.361(5)	2.374(5)
Ln(1B)-O(2B)	2.340(6)	2.333(6)	Ln(1D)-O(2D)	2.378(6)	2.379(6)
Ln(1B)-O(4 <sup>a</sup> )#2	2.421(5)	2.419(5)	Ln(1D)-O(4C)#4	2.398(5)	2.404(5)
Ln(1B)-O(1WB)	2.436(6)	2.442(5)	Ln(1D)-O(2WD)	2.410(6)	2.419(6)
Ln(1B)-O(4B)#1	2.445(5)	2.464(5)	Ln(1D)-O(4WD)	2.443(6)	2.449(6)
Ln(1B)-O(4WB)	2.453(6)	2.460(7)	Ln(1D)-O(4D)#3	2.494(5)	2.506(5)
Ln(1B)-O(3WB)	2.480(6)	2.493(5)	Ln(1D)-O(1WD)	2.517(6)	2.527(6)
Ln(1B)-O(2WB)	2.484(6)	2.515(6)	Ln(1D)-O(3D)#3	2.521(6)	2.527(6)
Ln(1B)-O(3B)#1	2.611(6)	2.629(5)	Ln(1D)-O(3WD)	2.532(6)	2.540(5)
			Ln(1A)-Ln(1B)	3.9458(9)	3.9644(6)
Ln(1C)-O(4D)#3	2.364(5)	2.375(5)	Ln(1C)-Ln(1D)	3.9482(9)	3.9647(6)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: (#1)  $-x + 2, y - 1/2, -z + 1$ ; (#2)  $-x + 1, y + 1/2, -z + 1$ ; (#3)  $-x, y - 1/2, -z$ ; (#4)  $-x + 1, y + 1/2, -z$ .

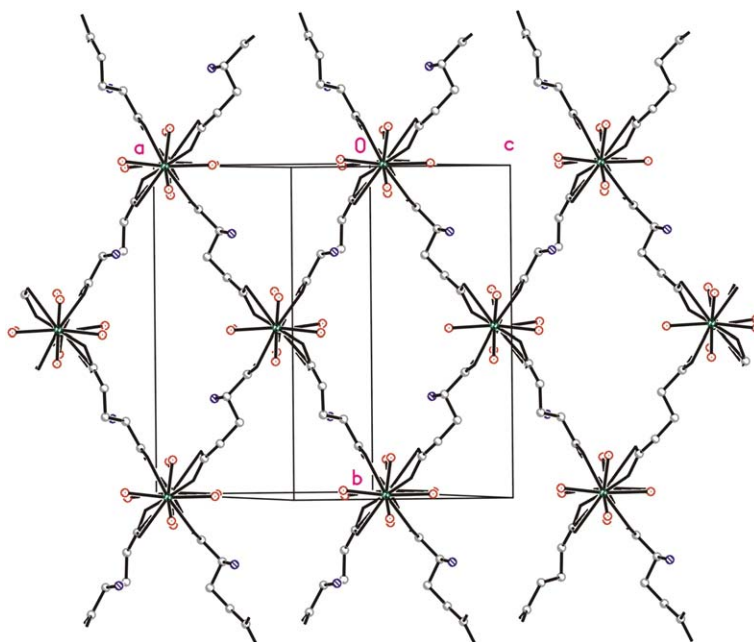


Fig. 1. Schematic view of one of the two independent 2D layers parallel to (001).

The analytical and spectroscopic data for the two complexes conform to a 1:1 metal to ligand stoichiometry. The IR spectra are almost identical within  $\pm 5 \text{ cm}^{-1}$ , suggesting similar structures for the two compounds. The spectra show changes in the position and profiles of some bands as compared to those in the free L-Glu. Major changes correspond to bands assigned to the carboxylate and aminium groups in amino acids [21], suggesting their participation in the bond scheme upon Ln(III) coordination. A detailed assignment of the bands is difficult particularly in the  $1700\text{--}1200 \text{ cm}^{-1}$  area in which the  $\text{NH}_3^+$  and  $\text{CH}_2$  deformations and  $\text{COO}^-$  stretching modes are strongly coupled. X-ray data show that compounds **1** and **2** are isostructural, and crystallize in the monoclinic space group  $P2_1$  as 2D polymers. Selected bond distances are presented in Table 2. Because the ionic radius of Gd(III) is

slightly shorter than that of the Eu(III) ion, all metal–ligand bonds in **2** are shorter than the corresponding bonds in **1**. However, the bond angles are nearly the same for **1** and **2** (see Supplementary Information). In what follows, only the Gd compound will be discussed, taken as representative of both. The structure can be described as a stacking of bidimensional polymeric arrays parallel to the (001) plane, containing gadolinium cations connected by glutamate anions.

There are two independent, almost identical, arrays in the structure containing gadolinium atoms Gd1A, Gd1B in one layer and Gd1C, Gd1D in the other layer, respectively. Fig. 1 presents a simplified view of one of the two independent 2D arrays, where all the hydrogen atoms, the perchlorate anions and the hydration water molecules have been omitted for clarity. Figs. 2a and b show, in turn,

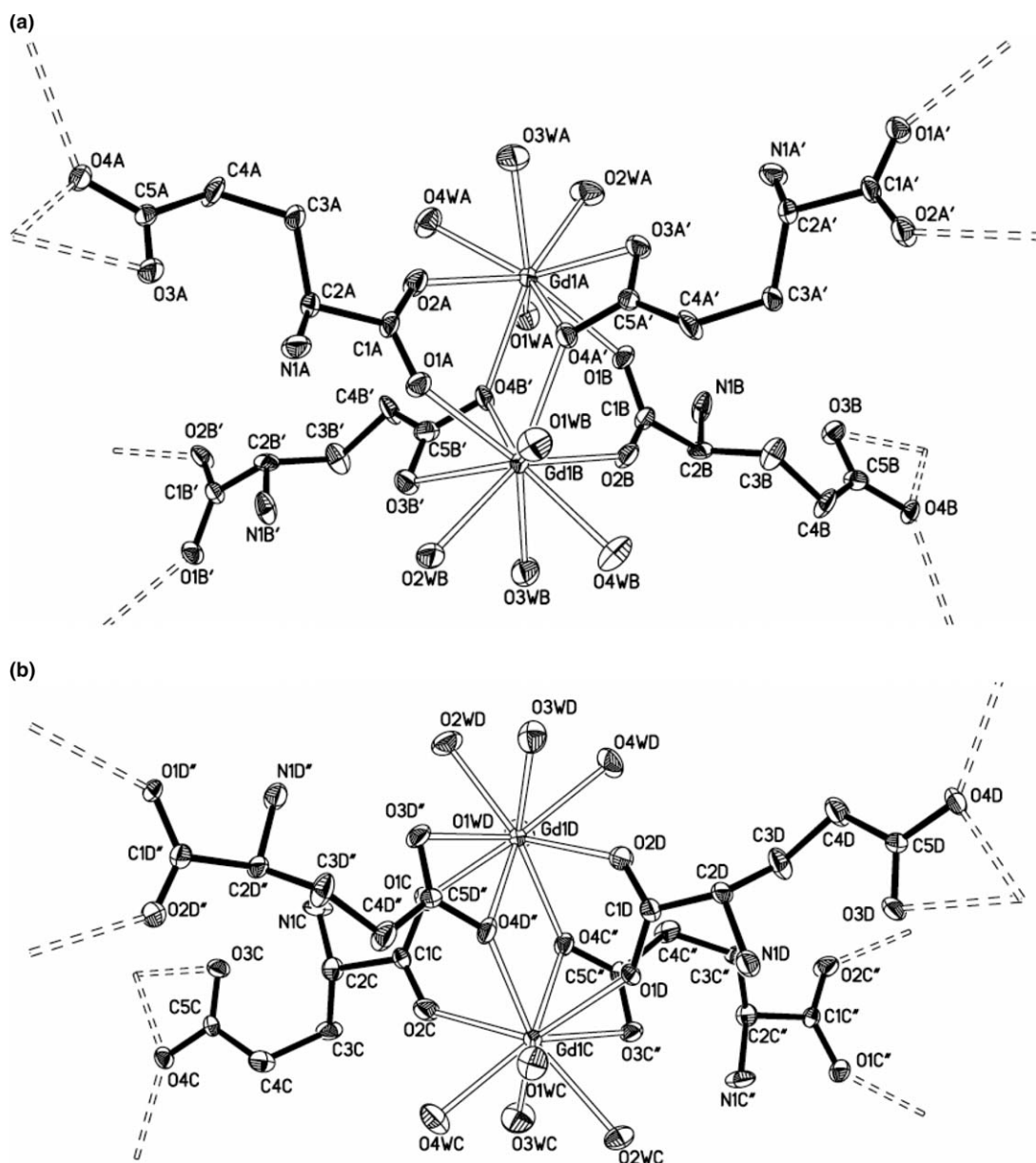


Fig. 2. The two independent  $[\text{Gd}_2(\text{L-Glu})_2(\text{H}_2\text{O})_8]^{4+}$  dinuclear units building up the structure.

the almost identical  $[\text{Gd}_2(\text{L-Glu})_2(\text{H}_2\text{O})_8]^{4+}$  dinuclear units which represent the elemental building blocks of the 2D arrays. The two gadolinium atoms are linked by four bridges provided by four carboxylate groups, defining a quasi centrosymmetric environment. Two of these bridges are provided by zwitterionic carboxylate groups ( $\text{H}_3\text{N}^+-\text{CHR}-\text{COO}^-$ ) through full carboxylate units in a  $\text{Gd}-\text{O}3-\text{C}5-\text{O}4-\text{Gd}$  scheme, while the other two involve a single carboxylate oxygen ( $\text{Gd}-\text{O}1-\text{Gd}$ ) from the terminal L-Glu  $\text{COO}^-$  groups. The carboxylate units providing these latter bridges behave as chelating towards one of the gadolinium cations (A,C) and monodentate towards the others (B,D). This type of interaction results in very similar  $\text{Gd}\cdots\text{Gd}$  distances in the two dinuclear units (3.946(1) and 3.948(1) Å for Gd1A,Gd1B and Gd1C,Gd1D, respectively). The contacts with four L-Glu residues provide each gadolinium atom with five out of its nine coordination sites, the remaining four being provided by aqua molecules (16 in all) O1WX to O4WX, X: A to D (see Fig. 2).

The 2D Gd-L-Glu sheets, shown in Fig. 1, extend parallel to (001), at heights  $z \sim 0.5$  for Gd1A,Gd1B and  $z \sim 0, 1$  for Gd1C,Gd1D. The space in between is filled with perchlorate counterions and hydration water molecules, see Fig. 3. The hydrogen bonding scheme involving  $\text{O}-\text{H}\cdots\text{O}$  bonds could only be inferred through the  $\text{O}\cdots\text{O}$  short contacts, as the hydrogen positions of the donor water molecules were almost impossible to determine confidently due to the presence of the heavy cationic species

and the poor crystallinity of the samples. Additional H-bonds of the intramolecular type involve one of the hydrogens of the  $\text{NH}_3^+$  group (H1XC, X: A to D) with the  $\gamma$ -carboxylate oxygen (O3X) in a  $\text{N}1\text{X}-\text{H}1\text{XC}\cdots\text{O}3\text{X}$  H-bond, which is almost identical in all moieties, as shown by the tight range of distances and angles displayed (viz.,  $\text{H}1\text{XC}\cdots\text{O}3\text{X}$ : 1.89–1.99 Å;  $\text{N}1\text{X}\cdots\text{O}3\text{X}$ : 2.744(9)–2.756(8) Å,  $\text{N}1\text{X}-\text{H}1\text{XC}\cdots\text{O}3\text{X}$ : 142–154°). The interaction defines a closed  $\text{C}2-\text{C}3-\text{C}4-\text{C}5-\text{O}3\cdots\text{N}1$  loop in the molecule and the overall planarity of the cation. The remaining hydrogens in each aminium group, in turn, make weak intermolecular contacts either to neighbouring water molecules or to vicinal perchlorates, thus providing to the packing stability. The initial L-character of the glutamate ligand has been kept throughout the synthesis process (final Flack parameters: 0.001(19) and 0.015(11), respectively). In fact, the non-centrosymmetric character of the dimeric units in the structure is a clear evidence of the chirality of the L-glutamic acid. In a racemic crystal, the effective number of sites is reduced by a factor of two, as reported for  $[\text{Ln}_2(\text{DL-Glu})_2(\text{H}_2\text{O})_8] \cdot 4(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ , Ln = Ho and Dy [16,17].

The EPR spectrum of complex 1 at room temperature shows a nearly symmetric broad band centered at  $g = 2$  with a peak-to-peak width of 66 mT, plus a second weak peak at about 100 mT, which is attributed to the low field turning point of “forbidden” transitions  $\Delta M = \pm 2$  [22]. As described recently [23], the width of the central peak can be

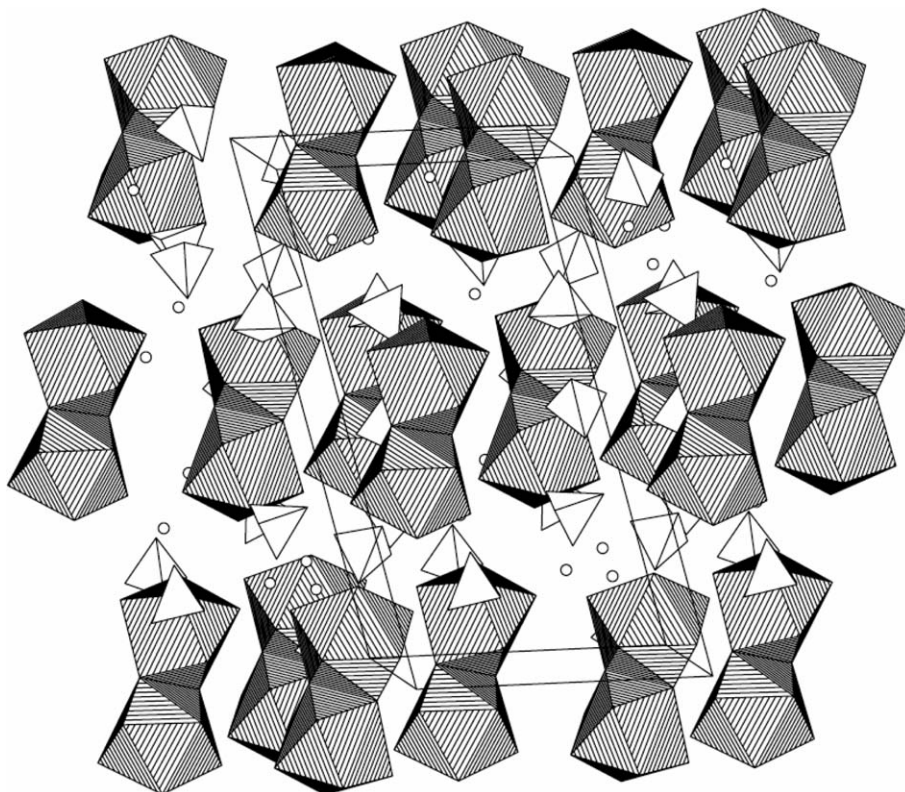


Fig. 3. Sideways view of the structure in a polyhedral representation, showing the stacking layers. Note the perchlorate counterions and hydration water molecules filling preferentially the interlayer spacing.

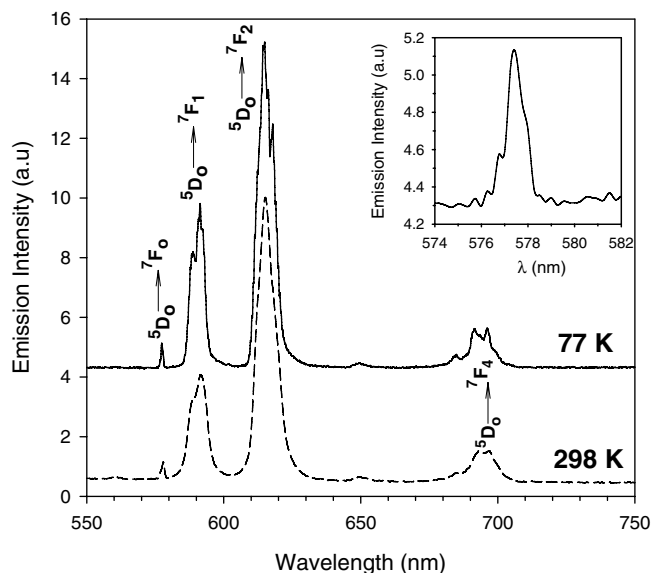


Fig. 4. Luminescence spectra of solid  $[\text{Eu}_2(\text{L-Glu})_2(\text{H}_2\text{O})_8] \cdot 4(\text{ClO}_4) \cdot 2.5\text{H}_2\text{O}$  at 298 and at 77 K.

assigned to the dipolar and exchange interactions within the dinuclear unit, acting on the zero field splitting of the Gd(III) ions. However, the distance between the dinuclear units is only a factor of  $\sim 2$  larger than that within these units, and the interdimeric dipolar interactions produce a 3D magnetic network that destroys any structure of the resonance.

The luminescence emission spectrum of compound **2** in solid state was measured down to 77 K (see Fig. 4). Bands centered at 577, 590, 615 and 695 nm correspond to the Eu(III) metal centered transitions ( $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ) for  $J = 0, 1, 2,$  and  $4,$  respectively [17]. The presence of the  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  band and the high intensity ratio of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2/{}^5\text{D}_0 \rightarrow ^7\text{F}_1$  bands are an indication that the Eu(III) ions are located in a low symmetry site [9,24,25]. Moreover, the observed splitting in the non-degenerate  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  band (see inset in Fig. 4) is a strong evidence that the Eu(III) ions are located in, at least, two different sites. This is consistent with our structural results that show four different sites in the unit cell.

Thus, the terminal  $\gamma$ -carboxylate group in L-glutamic acid determines the formation of the well-defined 2D infinite planes in the Ln/L-Glu complexes (Ln = Pr, Nd, Eu, Gd, Dy and Ho). Substitutions of the Ln metal centers provide mechanisms for manipulating the materials magnetic or optical properties and also to study the different properties of the Ln's in an essentially identical L-Glu network.

## Acknowledgments

We thank the Spanish Research Council (CSIC) for providing some of us with free-of-charge licenses to the CSD system. The work at INQUIMAE has been supported by PIP 02568 and PIP 5274. The work at UNL was supported by grants CAI+D-UNL, PIP 5274 and ANPCyT PICT 06-13782 and the work in Chile by Project CONICYT-FON-

DAP 11980002. M.P. and R.C. are members of CONICET.

## Appendix A. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication #CCDC 294544 (**1**), #CCDC 294543 (**2**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or [www:http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

## References

- [1] D. Tsuchiya, N. Kunishima, N. Kamiya, H. Jingami, K. Morikawa, Proc. Natl. Acad. Sci. USA 99 (5) (2002) 2660.
- [2] J.-C.G. Bünzli, C. Piquet, Chem. Rev. 102 (2002) 1897.
- [3] H. Tsukube, S. Shinoda, Chem. Rev. 102 (2002) 2389.
- [4] D. Parker, R.S. Dickins, H. Puschmann, C. Crossland, S.A.K. Howard, Chem. Rev. 102 (2002) 1977.
- [5] Z. Zhang, S. Nahir, T.J. McMurry, Curr. Med. Chem. 12 (7) (2005) 751.
- [6] Z. Dauter, M. Dauter, K.R. Rajashankar, Acta Crystallogr., Sect. D 56 (2000) 232.
- [7] R.A.P. Nagem, Z. Dauter, I. Polikarpov, Acta Crystallogr., Sect. D 57 (2001) 996.
- [8] J.-C.G. Bünzli, in: J.-C.G. Bünzli, G.R. Chopin (Eds.), Lanthanide Probes in Life, Chemical and Earth Science, Elsevier, Amsterdam, 1989.
- [9] P. Gawryszewska, J. Sokolnicki, J. Legendziewicz, Coord. Chem. Rev. 249 (2005) 2489.
- [10] N.S. Ivey, E.N. Martin Jr., W.M. Scheld, B.R. Nathan, J. Neurosci. Methods 142 (1) (2005) 91.
- [11] S.B. Gabelli, M.A. Bianchet, M.J. Bessman, M. Amzel, Nat. Struct. Biol. 8 (2001) 467.
- [12] C. Kremer, J. Torres, S. Domínguez, A. Mederos, Coord. Chem. Rev. 249 (2005) 567.
- [13] X. Li, K. Pan, Jiegou Huaxue (J. Struct. Chem.) 4 (1985) 75.
- [14] R.S. Dickins, A.S. Batsanov, J.A.K. Howard, D. Parker, H. Puschmann, S. Salamano, Dalton Trans. (2004) 70.
- [15] I. Csoregh, P. Kierkegaard, J. Legendziewicz, E. Huskowska, Acta Chem. Scand. Sect. A 41 (1987) 453.
- [16] J. Torres, S. Kramer, H. Pardo, L. Suescun, A. Mombrú, J. Castiglioni, S. Domínguez, A. Mederos, E. Kremer, J. Mol. Struct. 669 (2003) 99.
- [17] I. Csoregh, M. Czugler, P. Kierkegaard, J. Legendziewicz, E. Huskowska, Acta Chem. Scand. Sect. A 43 (1989) 735.
- [18] G.M. Sheldrick, SHELXL 97, Programs for Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1977.
- [19] F.H. Allen, Acta Crystallogr., Sect. B 58 (2002) 380.
- [20] A.G. Orpen, Acta Crystallogr., Sect. B 58 (2002) 398.
- [21] N.P.J. Roeges, A Guide to the Complete Interpretation of the Infrared Spectra of Organic Structures, Wiley, Chichester, England, 1994.
- [22] J.A. Weil, J.R. Bolton, J.E. Wertz, Electron Paramagnetic Resonance, Elemental Theory and Practical Applications, Wiley, New York, 1994, p. 165.
- [23] R. Baggio, R. Calvo, M.T. Garland, O. Peña, M. Perec, A. Rizzi, Inorg. Chem. 44 (2005) 8979.
- [24] M. Albin, R.R. Wright Jr., W.D. Horrochs, Inorg. Chem. 24 (1985) 2491.
- [25] P.P. Gawryszewska, L. Jerzykiewicz, P. Sobota, J. Legendziewicz, J. Alloys Compd. 300–301 (2000) 275, and references therein.