



# Article One-Dimensional Gadolinium (III) Complexes Based on Alphaand Beta-Amino Acids Exhibiting Field-Induced Slow Relaxation of Magnetization

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Abstract: Gadolinium (III) complexes exhibiting slow relaxation of magnetization are uncommon and have been much less studied than other compounds based on anisotropic lanthanide (III) ions. We prepared two one-dimensional gadolinium (III) complexes based on  $\alpha$ -glycine (gly) and  $\beta$ -alanine ( $\beta$ -ala) amino acids, with the formula {[Gd<sub>2</sub>(gly)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>](ClO<sub>4</sub>)<sub>6</sub>·5H<sub>2</sub>O}<sub>n</sub> (1) and {[Gd<sub>2</sub>( $\beta$  $ala_{6}(H_{2}O)_{4}](ClO_{4})_{6}\cdot H_{2}O_{1}(2)$ , which were magneto-structurally characterized. Compounds 1 and 2 crystallize in the triclinic system (space group Pī). In complex 1, two Gd (III) ions are eightcoordinate and bound to six oxygen atoms from six gly ligands and two oxygen atoms from two water molecules, the metal ions showing different geometries (bicapped trigonal prism and square antiprism). In complex 2, two Gd (III) ions are nine-coordinate and bound to seven oxygen atoms from six  $\beta$ -ala ligands and two oxygen atoms from two water molecules in the same geometry (capped square antiprism). Variable-temperature dc magnetic susceptibility measurements performed on microcrystalline samples of 1 and 2 show similar magnetic behavior for both compounds, with antiferromagnetic coupling between the Gd (III) ions connected through carboxylate groups. Ac magnetic susceptibility measurements reveal slow relaxation of magnetization in the presence of an external dc field in both compounds, hence indicating the occurrence of the field-induced singlemolecule magnet (SMM) phenomenon in both 1 and 2.

**Keywords:** amino acids; glycine; β-alanine; gadolinium; metal complexes; crystal structure; magnetic properties; single-molecule magnet

# 1. Introduction

Since the discovery of the mononuclear phthalocyanine-based lanthanide (III) complexes, which exhibit the single-molecule magnet (SMM) phenomenon, in 2003 [1,2], many efforts have focused on the synthesis and development of lanthanide(III)-based complexes in order to study this singular magnetic behavior, which allows SMMs to become promising candidates for potential applications in high-density data storage, quantum computing, molecular refrigeration and spintronics investigations [3–8].

Heterometallic 3d–4f mixed systems, radical bridged compounds, mono- and polynuclear lanthanide (III) complexes containing highly anisotropic 4f ions, mainly Dy (III) and to a lesser extent Tb (III), Ho (III) and Er (III), were investigated during the last two decades in the field of molecular magnetism [9–17]. More recently, mononuclear SMMs, also known as single-ion magnets (SIMs), based on dysprosium metallocenes were reported displaying energy barriers of magnetization reversal exceeding the 1500 cm<sup>-1</sup> value and blocking temperatures as high as that of the liquid nitrogen (>77 K), which exemplify the current progress in this research area [18,19].



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). In comparison with other members of the lanthanides family, the Gd (III) ion has been largely ignored in this type of study. This metal ion is considered magnetically isotropic due to the half-occupied  $4f^7$  electron configuration and the lack of orbital contribution (S = 7/2, L = 0) with an  ${}^8S_{7/2}$  ground state and a spherical quadrupole moment. Hence, the number of reported Gd (III) complexes that exhibit slow relaxation of magnetization is quite scarce [20,21]. Nevertheless, in some cases, Gd (III) cations show a very low or negligible value of the zero-field splitting (*D*), which induces the occurrence of ac signals for complexes of this quasi-isotropic 4f metal ion. In this way, when an external magnetic field is applied, the degeneracy between energy levels can be removed and the Quantum Tunnelling of Magnetisation (QTM) can be suppressed, which could result in mixed mechanisms of spin–lattice, spin–phonon and spin–spin relaxations [20]. This fact makes this type of study on both new and old Gd(III) systems very appealing.

Herein, we report the synthesis, crystal structure and magnetic properties of two carboxylate-bridged Gd<sup>III</sup> 1D coordination polymers of the formula {[Gd<sub>2</sub>(gly)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>] (ClO<sub>4</sub>)<sub>6</sub>·5H<sub>2</sub>O}<sub>n</sub> (**1**) and {[Gd<sub>2</sub>( $\beta$ -ala)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>](ClO<sub>4</sub>)<sub>6</sub>·H<sub>2</sub>O}<sub>n</sub> (**2**) [gly =  $\alpha$ -glycine and  $\beta$ -ala =  $\beta$ -alanine]. To the best of our knowledge, no magneto-structural study on homometallic gadolinium (III) complexes based on these amino acids has been reported so far (Scheme 1).



Scheme 1. Molecular structure of the amino acids  $\alpha$ -glycine (A) and  $\beta$ -alanine (B).

#### 2. Results and Discussion

## 2.1. Synthetic Procedure

Compounds 1 and 2 are prepared from a mixture of  $Gd_2O_3$  and glycine (1)/ $\beta$ -alanine (2). Both mixtures react in an aqueous solution acidulated with perchloric acid. However, the employed crystallization technique was different. While for preparing 1 the reaction mixture was heated at 80 °C for 48 h and then cooled at a rate of 4.5 °C/h to room temperature, the reaction mixture that generates compound 2 was heated at 60 °C for 1h and the resulting solution was left to evaporate at room temperature for 2 weeks. It is important to mention that, although no problems were encountered in this work, care should be taken when using the potentially explosive perchlorate anion ( $ClO_4^-$ ), which comes from the perchloric acid.

#### 2.2. Description of the Crystal Structures

Crystal data and structure refinement parameters for **1** and **2** are summarized in Table 1, where we indicate that both compounds crystallize in the triclinic system with centrosymmetric space group Pī. A recent review of the Cambridge Structural Database (CSD) revealed that the crystal structures of **1** and **2** were previously deposited with identifiers UKIKIJ and TEHKUN, respectively. Nevertheless, they were collected at room temperature and were deposited with refinement and resolution levels lower than the ones reported in this work [22,23].

The crystal structures of **1** and **2** are better described as cationic dinuclear  $[Gd^{III}_2]^{6+}$  units which are connected through carboxylate groups from glycine (**1**) and  $\beta$ -alanine (**2**), forming one-dimensional  $\{[Gd^{III}_2]^{6+}\}_n$  systems, the positive charges being counterbalanced by means of  $ClO_4^-$  anions. H<sub>2</sub>O solvent molecules are also present in their crystal structure (Figure 1).

Compound	1	2		
CIF	2149741	2149742		
Formula	C <sub>12</sub> H <sub>48</sub> Cl <sub>6</sub> N <sub>6</sub> O <sub>45</sub> Gd <sub>2</sub>	C <sub>18</sub> H <sub>52</sub> Cl <sub>6</sub> N <sub>6</sub> O <sub>41</sub> Gd <sub>2</sub>		
$Fw/g mol^{-1}$	1523.76	1535.85		
Temperature/K	120 (2)	120 (2)		
Crystal system	Triclinic	Triclinic		
Space group	Pī	Pī		
a/Å	11.401 (1)	9.172 (1)		
b/Å	13.986 (1)	12.733 (1)		
c/Å	15.506 (1)	21.558 (1)		
$\alpha/^{\circ}$	96.47 (1)	76.39(1)		
β/°	102.59 (1)	81.26 (1)		
$\gamma/^{\circ}$	105.99 (1)	82.47 (1)		
$V/Å^3$	2280.1 (2)	2406.9 (2)		
Z	2	2		
$D_{\rm c}/{\rm g}{\rm cm}^{-3}$	2.219	2.119		
$\mu (Mo - K_{\alpha})/mm^{-1}$	3.370	3.187		
F (000)	1504	1520		
Goodness-of-fit on $F^2$	1.013	0.989		
$R_1 [I > 2\sigma(I)]/all data$	0.0160/0.0175	0.0274/0.0302		
$wR_2 [I > 2\sigma(I)]/all data$	0.0417/0.0426	0.0741/0.0760		



CIF in Supplementary Materials.





In complex 1, two Gd<sup>III</sup> ions of the dinuclear  $[Gd_2(gly)_6(H_2O)_4]^{6+}$  unit are linked between them through four bridging carboxylate groups of four glycinate ligands (gly). These two Gd<sup>III</sup> ions are separated by a distance of 4.223(1) Å. Another two glycinate ligands connect these two Gd<sup>III</sup> ions to adjacent dinuclear units with separations of 5.229 (1) [Gd (1)…Gd (1a); (a) = 2 - x, 1 - y, 1 - z] and 5.135 (1) Å [Gd (2)…Gd (2b); (b) = 3 - x, 2 - y, 2 - z], thus generating a 1D {[Gd<sup>III</sup><sub>2</sub>]<sup>6+</sup>}<sub>n</sub> chain (Figure 2). Each Gd<sup>III</sup> ion of the dinuclear [Gd<sub>2</sub>(gly)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>6+</sup> unit is eight-coordinate and bonded to six oxygen atoms from six glycinate ligands and two oxygen atoms of two water molecules (Figure 1).



**Figure 2.** View of the one-dimensional motif of the homometallic  $\{[Gd_2(gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O\}_n$  chain in **1**. Perchlorate anions and non-coordinating water molecules were omitted for clarity. Colour code: violet, Gd; red, O; blue, N; grey, C; white, H.

The Gd–O bond lengths exhibit an average value of 2.419 (1) Å, which is somewhat shorter than that of the Gd–Ow bond lengths [2.506 (1) Å] [24]. The glycinate ligands are present in their zwitterionic form with C–C, C–N, and C–O bond lengths, which are in agreement with those found in the literature for similar lanthanide-based complexes [25,26].

In the packing of 1, the cationic  $\{[Gd^{III}_2]^{6+}\}_n$  chains are intercalated by  $ClO_4^-$  anions. The shortest interchain  $Gd\cdots Gd$  distance is approximately 11.0(1) Å. The dinuclear  $[Gd_2(gly)_6(H_2O)_4]^{6+}$  units in the chains of 1 are connected through H-bonding interactions, which involve coordinated water molecules [O (1w) $\cdots$ O (2wa) and O (3w) $\cdots$ O (4wb) distances of 2.844 (1) and 2.780 (1) Å, respectively]. Further H-bonding interactions generated by protonated  $-NH_2$  groups of the glycinate ligands and  $ClO_4^-$  anions link the  $\{[Gd^{III}_2]^{6+}\}_n$  chains in the structure of 1, as previously reported in the study of other SMMs structures [27–29].

In complex **2**, two Gd<sup>III</sup> ions are connected between them through four bridging carboxylate groups from four  $\beta$ -alanine ( $\beta$ -ala) ligands to form the dinuclear [Gd<sub>2</sub>( $\beta$ -ala)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>6+</sup> unit. The two Gd<sup>III</sup> ions are distanced from each other by an average separation of ca. 4.008 (1) Å (Figure 1), (the symmetry codes for the Gd (1)…Gd (1a) and Gd (2)…Gd (2b) distances being (a) = -x, 1 - y, -z and (b) = 1 - x, - y, 1 - z, respectively). Additional  $\beta$ -ala ligands link adjacent dinuclear units with separations of 5.196 (1) [Gd (1)…Gd (1c); (c) = 1 - x, 1 - y, -z] and 5.203 (1) Å [Gd (2)…Gd (2d); (d) = 2 - x, - y, 1 - z], generating a cationic 1D coordination polymer that grows along the crystallographic a-axis (Figure 3).



**Figure 3.** View of the one-dimensional motif of the homometallic  $\{[Gd_2(\beta - ala)_6(H_2O)_4](ClO_4)_6 \cdot H_2O)\}_n$  chain in **2**. Perchlorate anions and non-coordinating water molecules were omitted for clarity. Colour code: violet, Gd; red, O; blue, N; grey, C; white, H.

Each Gd<sup>III</sup> ion in **2** is nine-coordinate and bonded to seven oxygen atoms from six carboxylate groups of  $\beta$ -ala ligands and two oxygen atoms of two water molecules (Figure 1). The average value of the Gd–O bond lengths [2.388 (1) Å] is shorter than that of the Gd–Ow

bond lengths [2.522 (1) Å]. The  $\beta$ -ala ligands are coordinated in **2** as zwitterionic molecules and the values of the C–C, C–N, and C–O bond lengths agree with those found in the literature for similar complexes based on other lanthanide (III) ions [26,30].

In the packing of **2**, the cationic  $\{[Gd^{III}_2]^{6+}\}_n$  chains and  $ClO_4^-$  anions are arranged in an alternate way. They are linked through intermolecular H-bonding interactions involving non-coordinated water molecules and protonated  $-NH_2$  groups of  $\beta$ -ala ligands. The shortest interchain Gd…Gd distance in **2** is approximately 11.0 Å, which is for the Gd (2)…Gd (1c) separation. The supramolecular structure of **2** is generated through additional H-bonding interactions.

# 2.3. Analysis of the Polyhedral Structures

The coordination environment and geometry of the Gd<sup>III</sup> ions in **1** and **2** were further analyzed through the SHAPE program [31–33]. In **1**, the two Gd<sup>III</sup> ions show a coordination number equal to eight (Figure 1). The lower computed value for Gd (1) was 0.732, which was associated with a bicapped trigonal prism (BCTPR) geometry (Table 2). For Gd (2), however, a value of 0.915 was assigned to a square antiprism (SAPR) geometry (Figure 4 and Table 2). These features would suggest different geometries for the metal centers Gd (1) and Gd (2) in compound **1** (Figure 4).

**Table 2.** Selected values for possible geometries with coordination number (CN) equal to 8 obtained through the SHAPE program and from structural parameters of complex 1<sup> a</sup>.

Metal Ion	HBPY	CU	SAPR	TDD	JGBF	JETBPY	BTPR	JSD	TT
Gd(1)	17.116	11.317	1.254	1.763	13.137	27.406	0.732	3.440	11.813
Gu(2)	13.944	9.330	0.915	2.077	12.404	20.179	1.107	3.889	9.904

<sup>a</sup> HBPY: Hexagonal bipyramid (D<sub>6h</sub>); CU: Cube (Oh); SAPR: Square antiprism (D<sub>4d</sub>); TDD: Triangular dodecahedron (D<sub>2d</sub>); JGBF: Johnson gyrobifastigum (D<sub>2d</sub>); JETBPY: Johnson elongated triangular bipyramid (D<sub>3h</sub>); BTPR: Biaugmented trigonal prism (C<sub>2v</sub>); JSD: Snub diphenoid (D<sub>2d</sub>); TT: Triakis tetrahedron (Td).



**Figure 4.** Polyhedral view of the coordination sphere around the gadolinium (III) ions of the dinuclear  $[Gd^{III}_2]^{6+}$  unit in complex 1 [Gd (1), (left); Gd (2) (right)].

Unlike **1**, the two Gd<sup>III</sup> ions of the dinuclear  $[Gd^{III}_2]^{6+}$  unit in compound **2** exhibit a coordination number equal to nine (Figure 1). The lower SHAPE values computed for these two Gd<sup>III</sup> ions were 1.117 and 1.208 for Gd (1) and Gd (2), respectively (Table 3). These calculated values were assigned to a capped square antiprism (CSAPR) geometry (Figure 5), hence indicating the same geometry for the Gd<sup>III</sup> ions in the dinuclear  $[Gd^{III}_2]^{6+}$  unit of **2**.

**Table 3.** Selected values for possible geometries with coordination number (CN) equal to 9 obtained through the SHAPE program and from structural parameters of complex **2**<sup>*a*</sup>.

Metal Ion	HPY	JTC	JCCU	CSAPR	JTCTPR	TCTPR	JTDIC	HH	MFF
Gd(1)	19.213	15.400	10.340	1.117	2.255	1.543	12.866	10.100	1.368
Gd(2)	18.545	14.843	10.477	1.208	2.134	1.561	13.375	9.502	1.489

<sup>a</sup> HPY: Heptagonal bipyramid (D<sub>7h</sub>); JTC: Johnson triangular cupola ( $C_{3v}$ ); JCCU: Capped cube ( $C_{4v}$ ); CSAPR: Spherical capped square antiprism ( $C_{4v}$ ); JTCTPR: Tricapped trigonal prism ( $D_{3h}$ ); TCTPR: Spherical tricapped trigonal prism ( $D_{3h}$ ); JTDIC: Tridiminished icosahedron ( $C_{3v}$ ); HH: Hula-hoop ( $C_{2v}$ ); MFF: Muffin (Cs).



**Figure 5.** Polyhedral view of the coordination sphere around the gadolinium (III) ions of the dinuclear  $[Gd^{III}_2]^{6+}$  unit in complex **2** [Gd (1), (**left**); Gd (2) (**right**)].

As shown in Tables 2 and 3, these computed values for 1 allow us to assign the  $C_{2v}$  and  $D_{4d}$  symmetries to the Gd (1) and Gd (2) ions, respectively, whereas both Gd<sup>III</sup> ions (Gd (1) and Gd (2)) exhibit  $C_{4v}$  symmetry in **2**. In any case, they would be approximate symmetries.

## 2.4. Magnetic Properties

Dc magnetic susceptibility measurements were carried out on microcrystalline samples of **1** and **2** in the 2–300 K temperature range and under an external magnetic field of 0.5 T. In order to keep the samples both immobilized and well isolated from the moisture of the air at all moments, the organic compound eicosene was used. The  $\chi_M T$  versus T plots ( $\chi_M$  being the molar magnetic susceptibility per two Gd<sup>III</sup> ions) for compounds **1** and **2** are given in Figure 6. At room temperature, the  $\chi_M T$  values are ca. 15.7 (**1**) and ca. 15.9 cm<sup>3</sup>mol<sup>-1</sup>K (**2**), which are very close to that expected for two magnetically uncoupled Gd<sup>III</sup> ions (4f<sup>7</sup> ion with  $g_{Gd} = 2.0$ ,  $S_{Gd} = 7/2$  and  $L_{Gd} = 0$ ) [34]. Upon cooling, the  $\chi_M T$  values approximately follow the Curie law with decreasing temperature to ca. 20 K, before they decrease reaching minimum values of approximately 13.4 (**1**) and 14.0 cm<sup>3</sup>mol<sup>-1</sup>K (**2**) at 2 K. The decrease in the  $\chi_M T$  value observed for both compounds would likely be assignable to antiferromagnetic interactions and/or small zero-field splitting (ZFS) effects [20,21].

The field dependence of the molar magnetization (*M*) plots for **1** and **2** are given in the respective insets of Figure 6. The *M* values display a continuous increase with the applied magnetic field at 2 K. The higher *M* value is ca. 14.0  $\mu_B$  for both compounds, which is in agreement with those of similar Gd<sup>III</sup> compounds containing dinuclear units [35,36].



**Figure 6.** Thermal variation of the  $\chi_M T$  product for complexes 1 (left) and 2 (right). The solid red line represents the theoretical fit of the experimental data and the inset shows the M versus H plot at 2.0 K.

Taking into account the crystal structures described for **1** and **2**, which are made up of linked dinuclear Gd<sup>III</sup> units, we considered them as magnetically isolated dinuclear Gd<sup>III</sup>

systems. Thus, we performed the treatment of the experimental data of the  $\chi_M T$  versus *T* plots through the isotropic Hamiltonian of Equation (1):

$$\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 + \mu_B g H \hat{S} \tag{1}$$

The best least-squares fit gave the parameters J = -0.042 (1) cm<sup>-1</sup> and g = 2.003(1) with  $R = 4.7 \times 10^{-5}$  for **1**, and J = -0.030 (3) cm<sup>-1</sup> and g = 2.002 (1) with  $R = 5.2 \times 10^{-5}$  for **2** {*R* being the agreement factor defined as  $\sum_i [(\chi_M T)_i^{obs} - (\chi_M T)_i^{calcd}]^2 / [(\chi_M T)_i^{obs}]^2$ }. As shown in Figure 6, the calculated curves (solid red lines) reproduce the experimental magnetic data in the whole temperature range quite well. The sign and magnitude of the *J* values indicate the presence of weak antiferromagnetic exchanges between the Gd<sup>III</sup> ions connected through carboxylate bridges of the  $\alpha$ -glycine and  $\beta$ -alanine amino acids in **1** and **2**, respectively. As far as we know, these *J* values are the first ones reported for Gd<sup>III</sup> complexes based on these two amino acids. Nevertheless, they are in agreement with those previously reported for Gd<sup>III</sup> systems linked through similar carboxylate bridges [36].

Ac magnetic susceptibility measurements were performed on **1** and **2** in the temperature range of 2–25 K and in a 5.0 G ac field oscillating at different frequencies. No out-of-phase ac signals ( $\chi''_{M}$ ) were observed at  $H_{dc} = 0$  G, which may be caused by a very fast Quantum Tunnelling of Magnetization (QTM) in **1** and **2**. Nevertheless, out-of-phase ac signals were observed in both compounds when an external dc magnetic field (the optimal field being  $H_{dc} = 2500$  G) was applied. This applied dc magnetic field suppresses QTM and breaks the Kramer's doublet, leading to the observed slow relaxation [17,20,21]. In this way, both compounds show field-induced slow relaxation of magnetization, which is indicative of single-molecule magnet (SMM) behavior [4,7]. This magnetic relaxation observed for **1** and **2** was studied through both in-phase ( $\chi_{M}$ ') and out-of-phase ( $\chi_{M}$ '') ac susceptibilities versus frequency ( $\nu$ /Hz) plots, which are given in Figures 7 and 8, respectively. The experimental data of the maxima in **2** display higher intensity than those of **1**, even though similar relaxation dynamics could be a priori expected for both compounds.



**Figure 7.** Frequency dependence of the in-phase ac susceptibility signals under a dc field of 2500 G for **1** (left) and **2** (right).

The insets in Figure 8 show the  $\ln(\tau)$  versus 1/T curves for 1 and 2. In both compounds, the experimental data draw a straight line along the ranges of ca. 0.03–0.15 (1) and ca. 0.04–0.07 K<sup>-1</sup> (2) of the high-temperature region of 1 and 2, which connect with other straight-line behavior in the ranges of ca. 0.20–0.47 (1) and ca. 0.09–0.44 K<sup>-1</sup> (2) of the low-temperature region. In order to fit the experimental data of the ln ( $\tau$ ) versus 1/T plots, several relaxation mechanisms were considered for both compounds [7,9]. Nevertheless, the whole ln( $\tau$ ) versus 1/T curves were reasonably fitted through two mechanisms for the

relaxation of magnetization, namely, Orbach  $[\tau_0^{-1} \exp(-U_{eff}/k_B T)]$  and Raman  $[CT^n]$ , according to Equation (2):

$$\tau^{-1} = \tau_0^{-1} \exp\left(-U_{\rm eff}/k_{\rm B}T\right) + CT^n \tag{2}$$

The least-squares fit of the experimental data of **1** and **2** through Equation (2) leads to the following set of parameters:  $U_{eff} = 26.3 (2) \text{ cm}^{-1}$ ,  $\tau_0 = 3.1 (2) \times 10^{-6} \text{ s}$ ,  $C = 168 (5) \text{ s}^{-1}\text{K}^{-n}$  and n = 1.5 (2) for **1**, and  $U_{eff} = 7.8 (2) \text{ cm}^{-1}$ ,  $\tau_0 = 2.6 (1) \times 10^{-5} \text{ s}$ ,  $C = 2.6 (2) \text{ s}^{-1}\text{K}^{-n}$ , and n = 3.1 (2) for **2**. Although these values are the first ones reported for one-dimensional homometallic Gd<sup>III</sup> complexes based on these amino acids, they are close to those previously reported for similar Gd<sup>III</sup> complexes [12,13]. The values of the effective energy barrier ( $U_{eff}$ ) obtained for **1** and **2** are lower than those reported for the derivatives complexes containing Dy<sup>III</sup> ion [26]. Nevertheless, the U<sub>eff</sub> values reported for **1** and **2** should be carefully considered as they could not correspond to any excited Gd<sup>III</sup> states and therefore would not be real effective energy barrier values [13,21].



**Figure 8.** Frequency dependence of the out-of-phase ac susceptibility signals under a dc field of 2500 G for **1** (**left**) and **2** (**right**). The inset shows the ln ( $\tau$ ) versus 1/T plot with the fit considering the contribution of two mechanisms (Orbach + Raman).

The local symmetries displayed in the dinuclear Gd<sup>III</sup> units are  $C_{2v}$  and  $D_{4d}$  in **1** and  $C_{4v}$  in **2**. According to previous lanthanide (III) complexes studies, a priori, the local symmetry  $D_{4d}$  found in **1** would lead to better SMM properties [5–7], as observed for its  $U_{eff}$  value when compared with that of **2**, but this fact relies at last on the relative orientation of the magnetic anisotropy axes of all the spin carriers [26].

The  $\tau_0$  values obtained for 1 and 2, being approximately  $10^{-6}-10^{-5}$  s, are in agreement with those previously reported for single-ion and single-molecule magnets [13,17], which supports our consideration that the predominant magnetic behavior in both compounds would be that of dinuclear single-molecule magnets, rather than a single-chain magnet.

Finally, according to our results, the relaxation pathway for **1** and **2** should be a combination of different processes, namely, Orbach (at a higher temperature) and Raman (at a lower temperature), both of them involving two phonons. The reported *n* value for **1** ( $n \approx 2$ ) would indicate the presence at least of a phonon bottleneck effect, whereas the *n* value for **3** ( $n \approx 3$ ) would indicate the contribution of a Raman mechanism, as previously reported [37]. These *n* values suggest that only a direct process would not be operative in the relaxation dynamics of **1** and **2**. In any case, further detailed magnetic and theoretical studies performed on different Gd<sup>III</sup> complexes will be necessary to correctly understand the relaxation dynamics of Gd<sup>III</sup> SMMs.

#### 3. Experimental Section

#### 3.1. Preparation of the Complexes

3.1.1. Synthesis of  $\{[Gd_2(gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O\}_n$  (1)

A solvothermal reaction of Gd<sub>2</sub>O<sub>3</sub> (0.072 g, 0.20 mmol) and glycine (0.030 g, 0.40 mmol) was performed in an aqueous suspension (2 mL) acidulated with perchloric acid (1.0 mL, 2 M) at 80 °C for 48 h, followed by a cooling process at 4.5 °C/h to room temperature. Colourless parallelepipeds were obtained and were suitable for single-crystal X-ray diffraction studies. Yield: ca. 60%. Anal. Calcd. for  $C_{12}H_{48}N_6O_{45}Cl_6Gd_2$  (1): C, 9.5; H, 3.2; N, 5.5. Found: C, 9.9; H, 3.0; N, 5.3. SEM-EDAX: a molar ratio of 1:3 for Gd/Cl was found for 1. IR (KBr pellet): peaks associated mainly to the glycine ligand and also to the perchlorate anion are observed at 3407 (s), 3080(m), 3006 (m), 2781 (w), 2708 (w), 1628 (vs), 1609 (vs), 1570 (m), 1499 (m), 1466 (m), 1413 (m), 1335 (m), 1144 (vs), 1109 (vs), 1088 (s), 905 (m), 626 (s), 536 (w), 507 (w) cm<sup>-1</sup>.

# 3.1.2. Synthesis of $\{[Gd_2(\beta-ala)_6(H_2O)_4](ClO_4)_6 \cdot H_2O)\}_n$ (2)

A mixture of Gd<sub>2</sub>O<sub>3</sub> (0.090 g, 0.25 mmol) and  $\beta$ -alanine (0.022 g, 0.25 mmol) in an aqueous suspension (5 mL) acidulated with perchloric acid (1.0 mL, 2 M) was stirred and heated at 60 °C for 1h. The resulting solution was left to evaporate at room temperature for 2 weeks. Colourless needles were obtained, which were suitable for single-crystal X-ray diffraction. Yield: ca. 55%. Anal. Calcd for C<sub>18</sub>H<sub>52</sub>N<sub>6</sub>O<sub>41</sub>Cl<sub>6</sub>Gd<sub>2</sub> (2): C, 14.1; H, 3.4; N, 5.5. Found: C, 14.0; H, 3.3; N, 5.6. SEM-EDAX: a molar ratio of 1:3 for Gd/Cl was found for **2**. IR (KBr pellet): peaks associated to  $\beta$ -alanine ligand and perchlorate anion are observed at 3396 (s), 1622 (s), 1578 (s), 1460 (s), 1406 (m), 1336 (m), 1312 (w), 1264 (w), 1144 (vs), 1116 (vs), 1090 (s), 958 (m), 941 (w), 641 (m), 627 (s), 590 (w), 520 (w) cm<sup>-1</sup>.

#### 3.2. X-ray Data Collection and Structure Refinement

X-ray diffraction data collection on single crystals of dimensions  $0.18 \times 0.11 \times 0.09$ (1) and  $0.18 \times 0.09 \times 0.06 \text{ mm}^3$  (2) were collected on a Bruker D8 Venture diffractometer with PHOTON II detector and by using monochromatised Mo-K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$ Å). Crystal parameters and refinement results for 1 and 2 are summarized in Table 1. The structures were solved by standard direct methods and subsequently completed by Fourier recycling using the SHELXTL [38] software packages and refined by the full-matrix least-squares refinements based on F<sup>2</sup> with all observed reflections. The final graphical manipulations were performed with the DIAMOND [39] and CRYSTALMAKER [40] programs. CCDC 2,149,741 and 2,149,742 for 1 and 2, respectively.

#### 3.3. Physical Measurements

Elemental analyses (C, H, N) were performed in an Elemental Analyzer CE Instrument CHNS1100 and the molar ratio between heavier elements was found by means of a Philips XL-30 scanning electron microscope (SEM-EDAX), equipped with a system of X-ray microanalysis, in the Central Service for the Support to Experimental Research (SCSIE) at the University of Valencia. Infrared spectra (IR) of **1** and **2** were recorded with a PerkinElmer Spectrum 65 FT-IR spectrometer in the 4000–400 cm<sup>-1</sup> range. Variable-temperature, solid-state (dc and ac) magnetic susceptibility data were collected on Quantum Design MPMS-XL SQUID and Physical Property Measurement System (PPMS) magnetometers. Experimental magnetic data were corrected for the diamagnetic contributions of both the sample holder and the eicosene. The diamagnetic contribution of the involved atoms was corrected by using Pascal's constants [41].

#### 4. Conclusions

In summary, the synthesis, crystal structure and magnetic properties of two one-dimensional Gd<sup>III</sup> complexes based on the  $\alpha$ -glycine (gly) and  $\beta$ -alanine ( $\beta$ -ala) amino acids, with the formula {[Gd<sub>2</sub>(gly)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>](ClO<sub>4</sub>)<sub>6</sub>·5H<sub>2</sub>O}<sub>n</sub> (1) and {[Gd<sub>2</sub>( $\beta$ -ala)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>](ClO<sub>4</sub>)<sub>6</sub>·H<sub>2</sub>O}<sub>n</sub> (2), were reported. Their structures are described as cationic dinuclear [Gd<sup>III</sup><sub>2</sub>]<sup>6+</sup> units which

are connected through carboxylate groups from glycine (1) and  $\beta$ -alanine (2), forming one-dimensional {[Gd<sup>III</sup><sub>2</sub>]<sup>6+</sup>}<sub>n</sub> systems. Different symmetries of the Gd<sup>III</sup> ions, namely, C<sub>2v</sub> and D<sub>4d</sub> in 1 and C<sub>4v</sub> in 2, were found in the study of their coordination environment.

The investigation of the magnetic properties of **1** and **2** through dc magnetic susceptibility measurements reveals a similar magnetic behavior, with both compounds exhibiting weak antiferromagnetic exchange couplings between Gd<sup>III</sup> ions. In addition, ac magnetic susceptibility measurements show field-induced slow relaxation of magnetization for both **1** and **2**, which indicates that the single-molecule magnet (SMM) phenomenon takes place in these novel one-dimensional Gd<sup>III</sup> complexes.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics10030032/s1, CIF files 2149741 (1) and 2149742 (2).

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