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Novel unexpected Tb³⁺ coordination polymer containing two carboxylate ligands: Syntheses, structure and photoluminescent properties

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Abstract

Novel unexpected coordination polymer [Tb(PHTHGLY)(CBGLY)(H₂O)₂](H₂O)₃ complex containing simultaneously *N*-phthaloylglycinate and *N*-(2-carboxybenzoyl)glycinate ligands has been prepared and characterized by single crystal X-ray structure, thermogravimetric analysis and infrared spectroscopy. The X-ray crystal diffraction indicates that the Tb³⁺-complex crystallizes in a triclinic crystal system and space group $P\overline{1}$, forming a 1D polymer where carboxylate groups bridge the Tb³⁺ ions. The photoluminescence data revel that the ligands act as efficient "antennas" sensitizing the luminescence of the Tb³⁺ ion showing a strong green emission color arising from intraconfigurational ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ transitions (J = 0-6).

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Lanthanide complexes containing carboxylate ligands are the most largely investigated kinds of coordination compounds due to the higher thermal and luminescent stabilities, which make them potential candidates for organic electroluminescent devices (OLEDs) applications and as fluoroimmunoassay agents [1,2]. Since the emission mechanism of trivalent lanthanide ions (Ln^{3+}) is based on "antenna effect", aromatic carboxylate coordinated ligands act as sensitizers, absorbing and transferring energy efficiently to the excited levels of the Ln^{3+} ion. Additionally, carboxylate group may present various coordination modes, leading to formation of mononuclear, dinuclear, polymeric or network compounds [3]. The understandings of the structural and chemical factors that control the supramolecular chemistry of the carboxylate compounds are important for several areas such as optoelectronic, magnetism and catalysis [4].

Among carboxylate ligands the chemistry of N-phthaloylglycine derivatives of amino acids has attracted considerable attention because they are precursors in the synthesis of several compounds presenting biological and medical activity [5]. N-protected amino acids such as N-phthaloylglycine (PHTHGLY) and N-(2-carboxybenzoyl)glycine (CBGLY) may also act as versatile ligands, forming complexes with a variety of metal complexes. These molecules can be potentially coordinated to the metal ion through the carbonyl moiety(ies) or carboxylate groups. Recently, several papers have been concerned with describing the structure material based on transition metal ions such as zinc, nickel and copper containing phthaloylglycine (PHTHGLY) and its derivatives [6]. Generally, in those systems carboxylate groups are coordinated in a monodentate fashion, giving mononuclear compounds

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with moderately simple structures. However, due to the difference in some properties for Ln^{3+} ions, as compared with divalent transition metal ions, such as the higher electrostatic ligand-metal ion interaction and the higher and variable coordination number, a significantly different compound with more complicated features are expected.

To the best of our knowledge, no lanthanide crystal structure and spectroscopic studies of Ln^{3+} -complexes with the *N*-phthaloylglycine derivatives ligands have been reported. However, in this paper it has been reported the syntheses [7], characterization [8] and luminescence properties of a new Tb³⁺-complex containing two different N-protected glycinate, *N*-phthaloylglycinate (PHTHGLY) [9] and *N*-(2-carboxybenzoyl)glycinate (CBGLY). It also reports the systematic investigation of the structural properties of the Tb³⁺-compound.

Thermogravimetric analysis of {[Tb(PHTHGLY) (CBGLY)(H₂O)₂](H₂O)₃}_{∞} complex in the temperature range 25–950 °C is shown in Fig. 1. The TG curve shows weight losses in the 25–200 °C range with a total loss of 11.30% which can be ascribed to the removal of five water molecules (three of hydration and two of coordination). These data corroborate with the IR absorption and with the elemental analysis results. The second step presents successive weight loss of which is assigned to decomposition of the coordinated PHTHGLY and CBGly ligands.

Fig. 2 displays the structure of the Tb^{3+} -complex determined by X-ray crystallography which is constituted of a 1D polymer leading to a chain-like formulation {[Tb(PHTHGLY)(CBGLY)₂(H₂O)](H₂O)₃}_{∞} [10]. In this case, the carboxylate group that belongs to PHTHGLY ligand is coordinated to the Tb³⁺ ion in both chelating and bridging fashion. It is interesting to mention that PHTHGLY and their derivatives ligands are generally coordinated to the divalent transition metal ions in a monodentate style [6]. Among other factors, this behavior is probably due to the non-directional character of the oxygen atoms-lanthanide ion bonds that are predominantly



Fig. 1. TG curve of the [Tb(PHTHGLY)(CBGLY)(H₂O)₂](H₂O)₃ complex under a N_2 atmosphere and using heating rate of 10 °C/min.



Fig. 2. Structure of the [Tb(PHTHGLY)(CBGLY)(H₂O)₂](H₂O)₃ complex, the displacement ellipsoids are drawn on 50% probability level. All hydrogen atoms, lattice water molecules and phthaloyl groups were omitted for clarity. Selected bond lengths (Å), and angles (°): bond lengths. Tb-O6 2.245(3), Tb-O5 2.341(3), Tb-O7 2.342(2), Tb-O4 2.349(3), Tb-O1W 2.354(3), Tb-O3W 2.407(3), Tb-O2 2.505(3), Tb-O7 2.505(3), Tb-Tb 4.0094(3). Bond angles O6-Tb-O5 97.03(12), O6-Tb-O7 162.32(12), O5-Tb-O7 84.87(11), O6-Tb-O4 92.35(10), O5-Tb-O4 149.29(10), O7-Tb-O4 77.83(9), O6-Tb-O1W 81.97(14), O5-Tb-O1W 74.61(11), O7-Tb-O1W 81.60(12), O4-Tb-O1W 77.88(11), O6-Tb-O3W 87.65(12), O5-Tb-O3W 139.21(10), O7-Tb-O3W 102.43(10), O4-Tb-O3W 70.12(10), O1W-Tb-O3W 145.86(11), O6-Tb-O2 77.13(10), O5-Tb-O2 72.60(10), O7-Tb-O2 119.93(9), O4-Tb-O2 138.10(10), O1W-Tb-O2 138.23(11), O3W-Tb-O2 69.04(10), O6-Tb-O7 128.88(10), O5-Tb-O7 71.75(10), O7-Tb-O7 68.45(10), O4-Tb-O7 122.97(9), O1W-Tb-O7 136.28(11), O3W-Tb-O7 73.94(10), O2-Tb-O7 51.78(8), O6-Tb-Tb 161.60(8), O5-Tb-Tb 75.65(8), O7-Tb-Tb 35.54(6), O4-Tb-Tb 102.52(6), O1W-Tb-Tb 111.49(10), O3W-Tb-Tb 87.30(8), O2-Tb-Tb 84.54(6), O7–Tb–Tb 32.91(6). Symmetry codes: (i) x, y, z, (ii) -x, -y, -z.

ionic and due to the higher radius of the trivalent lanthanide ion as compared with divalent metal transition ions.

The most important feature of this complex is that the carboxylate groups belonging to CBGLY ligand are coordinated to the Tb^{3+} ion by two different ways. As it can be seen, aromatic carboxylate group is coordinated in a bridging mode whereas carboxylate group belonging to glycine moiety is presented as a monodentate group. However, the non-coordinated oxygen atom of the latter is hydrogen bonded to the lattice water. The structure also shows that all coordinated and non-coordinated water molecules have extensive hydrogen bonds. The existences of hydrogen bonding interactions between adjacent units form the 2D supramolecular infinite chain hydrogen bonding. Additionally, it is observed that the carbonyl groups belonging to PHTHGLY ligand are hydrogen-bonded to the N-H group of the CBGLY ligand and to one lattice water (Fig. 3a). The donor-acceptor bond angles and distances are listed in Table 1. The N-phthaloylglycinate ligands of



Fig. 3. (a) Intramolecular hydrogen bonded self-assembly of $[Tb(PHTHGLY)(CBGLY)(H_2O)_2](H_2O)_3$ complex. (b) Intermolecular hydrogen bonded self-assembly of $[Tb(PHTHGLY)(CBGLY)(H_2O)_2](H_2O)_3$ complex.

the one-dimensional layers are pointed towards neighboring layers, leading to weak interactions through π - π stacking (Fig. 4). The distance between the π -stacked rings is around 3.566 Å.

According to the coordination modes of ligands, eight oxygen atoms are coordinated to Tb^{3+} ion (three from CBGLY, three from PHGLY and two from water molecules) leading to a coordination polyhedra that can be described as a distorted dodecahedron. These polyhedra are connected to each other through the O7 and O7A atoms belonging to phthaloylglycinate ligand.

The shortest interatomic distance in the coordination polyhedra of Tb^{3+} is observed for Tb–O6 with value of 2.245 Å, while the longest is presented for Tb–O2 and Tb–O7 with values around 2.505 Å. As it can be seen,

one oxygen atom of the bridging carboxylate presents shorter interatomic distance than those involving the chelate bridging oxygen atoms. This behavior is similar to that shown in other Ln^{3+} complexes that present carboxylate groups coordinated to the metal ion as both chelates bridging and bridging fashions [11]. It is also interesting to notice that the distance Tb–O1W is shorter (2.354 Å) than Tb–O3W (2.407 Å), which is probably due to the presence of one (O1W–H1W–O11) and two (O1W–H1W–O2A and O1W–H1W–O8A) hydrogen bonding, respectively (Fig. 3b). The other Tb–O distances are around 2.3 Å.

The Tb–Tb distances in the {[Tb(PHTHGLY)-(CBGLY)(H₂O)₂](H₂O)₃} $_{\infty}$. polymer are equals to 4.0094(3) and 5.253 Å. Polyhedral representation of the compound is displayed in Fig. 4. It is also important to

Table 1
Selected hydrogen-bonding in [Tb(PHTHGLY)(CBGLY)(H ₂ O) ₂](H ₂ O) ₃ complex

Hydrogen bond	$d_{\mathrm{D-H}}(\mathrm{\AA})$	$d_{\mathbf{A}\cdots\mathbf{H}}$ (Å)	$d_{\mathbf{A}\cdots\mathbf{D}}$ (Å)	∠D–H···A (°)
O1W–H1W···O11(intramolecular)	0.85	1.993	2.714	142.1
O3W-H5W···O8 (intramolecular)	0.85	2.124	2.730	127.9
O3W-H6W···O2 (intramolecular)	0.85	2.423	2.785	106.4
N2–H1N2···O10 (intramolecular)	0.96	1.986	2.948	174.7
O12-H12W···O11 (intramolecular)	0.85	2.199	3.005	158.2
O12–H13X···O9 (intramolecular)	0.85	2.637	3.155	120.5
O3W–H6W···O13 ($-x + 1, -y + 1, -z + 1$)	0.85	2.619	3.011	109.5
O3W–H6W ···O12 ($-x + 1, -y + 1, -z + 1$)	0.85	2.184	2.670	116.2
O13–H15W···O11 $(-x+1, -y+2, -z+1)$	0.85	1.969	2.799	165.0
O12–H13X···O8 $(x, +y + 1, +z)$	0.85	2.208	2.884	136.4



Fig. 4. Polyhedral representation of $[Tb(PHTHGLY)(CBGLY)(H_2O)_2](H_2O)_3$ complex. Green polyhedra are $[TbO_8]$ unit, which are connected through carboxylate ligands. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

observe that the two polyhedra bridged by oxygen atoms belonging to the PHTHGLY ligand are equivalent by symmetry, consequently the Tb³⁺ atoms are also equivalent.

Fig. 5a shows the excitation spectrum of the Tb³⁺-complex recorded in the spectral range from 250 to 590 nm, with emission monitored on the hypersensitive ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition at 542 nm. This spectrum consists of a broad band in the spectral range from 250 to 370 nm, which is attributed to the $S_{0} \rightarrow S_{1}$ transitions of the PHTHGLY and CBGLY ligands. It is also observed narrow bands arising from 4f–4f transitions from the ground state ${}^{7}F_{6}$ level (nm) to the ${}^{5}L_{10}(369)$, ${}^{5}G_{6}(376)$, ${}^{5}D_{3}(388)$ and ${}^{5}D_{4}(488)$. However, the relative intensity of the broad band is higher than those centered on the Tb³⁺ ion, suggesting that the indirect excitation processes of the metal ion via chromophore groups from ligands are more operative.

The emission spectrum of Tb^{3+} -complex in the solid state at liquid nitrogen temperature is shown in Fig. 5b. This spectrum displays characteristic narrow emission bands assigned to the ${}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{J}$ transitions (J = 0, 1, 2, 3)

3, 4, 5 and 6), presenting the hypersensitive ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition as the most prominent which is extremely sensitive to chemical environment around Tb^{3+} ion. The emission spectrum also exhibits no bands arising from the ligands centered transitions, indicating there is an efficient intramolecular energy transfer from the carboxylate ligands to the Tb^{3+} ion. In spite of the larger distance from the aromatic chromophores moiety to the metal ion, this energy transfer is probably taken from the triplet $T(\pi,\pi^{*})$ of the ligands to the excited energy levels of the Tb^{3+} ion. The same behavior was observed for other Tb^{3+} -carboxylate complexes [11].

In summary, our study demonstrated that the Tb^{3+} ion forms a new unexpected compound with two different caboxylate ligand, *N*-phthaloylglycinate and *N*-(2-carboxybenzoyl)glycinate ligands. The photoluminescent data suggest that the ligands act as efficient "antennas" sensitizing the luminescence of the Tb^{3+} ion. Additionally, the synthesized complex can activate efficiently the luminescence of Tb^{3+} ions by the substitution of two water molecules



Fig. 5. (a) Excitation spectrum of $[Tb(PHTHGLY)(CBGLY)(H_2O)_2](H_2O)_3$ complex recorded with emission monitored at 542 nm, at 77 K. (b) Emission spectrum of $[Tb(PHTHGLY)(CBGLY)(H_2O)_2](H_2O)_3$ complex recorded with emission monitored at 542 nm, at 77 K.

by some organic ligand (example: sulfoxides, amides, heterocyclics, etc.) can increase the emission quantum yield, making the Tb-complex a potential candidate as emitter in photonic systems.

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Appendix A. Supplementary material

CCDC 635010 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche. 2007.04.013.

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- [7] Synthesis of the { $[Tb(PHTHGLY)(CBGLY)(H_2O)_2](H_2O)_3$ } complex: A mixture of the ligands N-phthaloylglycine (4.9 mmol, 1.0 g) and N-(2-carboxybenzoyl)glycine (4.9 mmol, 1.1 g) was dissolved in 30 mL of water at room temperature. A solution of NaOH was added dropwise to adjust pH to approximately 6.5. An aqueous solution of TbCl₃ · 6H₂O (4.985 mmol, 1.1 g,) was added dropwise to this solution and after five days colorless crystals were obtained. These crystals were filtered, washed with water and dried under vacuum to give the desired product (yields 85%). The composition of the complex was confirmed by elemental analysis. Anal. Calc. for TbO₁₃N₂C₂₀H₂₃: Tb, 23.57; C, 35.62; H, 3.44; N, 4.15. Found: Tb, 23.41; C, 35.53; H, 3.20; N: 4,14%. IR (KBr, cm⁻¹): 3564 m, 3554 m, 3064 m, 1774 m, 1711 s, 1634 s, 1568 s, 1439 s, 1410 s, 1385 m, 1292 m, 1115 m, 964 m, 750 m, 713 s, 630 m, 557 w, 428 w, 410 w (figure not shown). The broad band around 3554 cm⁻¹ is attributed to v(O-H) stretching, confirming the presence of water molecules in the lattice or coordinated to the terbium ion. On the other hand, the band at 3564 cm^{-1} can be ascribed to the stretching vibration of the amide NH group which belongs to the CBGLY ligand. IR spectrum of the Tb³⁺complex also shows unchanged asymmetric and symmetric stretching modes of ketonic carbonyl groups C=O at 1710 and 1770 cm⁻¹ respectively, indicating non-participation of these groups in the coordination to the Tb^{3+} ion. However, the most relevant bands to investigate the coordination mode of carboxylate ligands are the bands assigned to $v_s(C=O)$ and $v_{ass}(C=O)$. For Tb(PHTH-GLY)(CBGLY)(H_2O)_2](H_2O)_3\}_\infty polymer these bands from carboxylic groups are observed around 1420 and 1635 cm⁻¹ respectively. The $\Delta[v_{as}(C=0) - v_{s}(C=0)]$ around 200 cm⁻¹ clearly indicates chelating and bridging nature of the carboxylate groups 3.
- [8] Experimental: The PHTHGLY and CBGLY ligands were synthesized as described in Ref. [9]. The carbon and hydrogen percentages in the complexes were determined from elemental analyses, using a Perkin– Elmer model 240 microanalyzer, while the Tb³⁺ content was performed by complexometric titration with EDTA. The infrared absorption spectra were recorded in KBr pellets on a Bomen model MB-102 spectrophotometer in the range of 400–4000 cm⁻¹. The excitation and emission spectra at room (~298 K) and liquid nitrogen temperature were collected at an angle of 22.5° (front face) in a spectrofluorimeter (SPEX-Fluorolog 2) with double grating 0.22 m monochromator (SPEX 1680), and a 450 W Xenon lamp as excitation source. To eliminate the second-order diffraction of the source radiation, a cut-off filter was used in the measurements. All spectra were recorded using a detector mode correction. The luminescence decay curves of the emitting levels were measured using a phospho-

rimeter SPEX 1934D accessory coupled to the spectrofluorimeter. The luminescence instruments were fully controlled by a DM3000F spectroscopic computer program and the spectral intensities were automatically corrected for the photomultiplier response.

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- [10] Crystal data for ${[Tb(PHTHGLY)(CBGLY)(H_2O)_2](H_2O)_3}_{\infty}$ complex: Diffraction data of [Tb(PHTHGLY)(CBGLY)(H₂O)₂](H₂O)₃ complex were collected at room temperature with an Enraf-Nonius CAD4 Mach3 single crystal diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 298 K. The orientation matrix and cell dimensions were determined by least-square refinement of the angular positions of 25 reflections. The data were processed on a Pentium PC and corrected for absorption and Lorentz polarization effects. The structure of the [Tb(PHTH-GLY)(CBGLY)(H₂O)₂](H₂O)₃ complex was solved by Patterson method. Full-matrix least-squares refinement (on F²) with anisotropic thermal parameters for all non-hydrogens atoms was used. The H atoms were located on stereochemical grounds, and refined riding on carrier atom, with an isotropic displacement parameter of the atom to which they were attached. Space group, structure solution, refinement, molecular graphics and geometrical calculation have been

carried out with the SHELX-L97 [12] and ZORTEP [13] programs. PARST95 [14] and WinGX [15] were used to prepare material for publication. Crystallographic data for the structure C₂₀H₂₃N₂O₁₃Tb were, chemical_formula_weight = 658.32, *P*Ī, unit cell parameters: a = 9.079(9) Å, b = 10.186(6) Å, c = 14.673(6) Å, $\alpha = 109.15(8)^{\circ}$, $\beta = 94.39(5)^{\circ}$, $\gamma = 106.36(9)^{\circ}$, V = 1208.4 Å³, Z = 2, measurement temperature = 293(2), $D_c = 1.809$ Mg m⁻³, $\mu = 2.997$ mm⁻¹, F(000) = 652. θ Range data collection 2.24–25.60. Reflections collected were obtained from a total of 4845 and independent/ observed is 4540 ($R_{int} = 0.0212$) and 4346 measured reflections, respectively. Structure solution and refinement based on 4540 independent reflections. The Final *R* indices [$I > 2\sigma(I)$], $R_1 = 0.0270$ and $wR_2 = 0.0763$. *R* indices (all data), $R_1 = 0.0291$ and $wR_2 = 0.0823$, respectively.

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