

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* $\bar{1}$, forming a 1D polymer where carboxylate groups bridge the Tb³⁺ ions. The photoluminescence data reveal that the ligands act as efficient “antennas” sensitizing the luminescence of the Tb³⁺ ion showing a strong green emission color arising from intraconfigurational ⁵D₄ → ⁷F_{*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 (Ln³⁺) is based on “antenna effect”, aromatic carboxylate coordinated ligands act as sensitizers, absorbing and transferring energy efficiently to the excited levels of the Ln³⁺ 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 Tb^{3+} -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 Tb^{3+} -compound.

Thermogravimetric analysis of $\{[\text{Tb}(\text{PHTHGLY})(\text{CBGLY})(\text{H}_2\text{O})_2](\text{H}_2\text{O})_3\}_\infty$ 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 $\{[\text{Tb}(\text{PHTHGLY})(\text{CBGLY})_2(\text{H}_2\text{O})](\text{H}_2\text{O})_3\}_\infty$ [10]. In this case, the carboxylate group that belongs to PHTHGLY ligand is coordinated to the Tb^{3+} 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

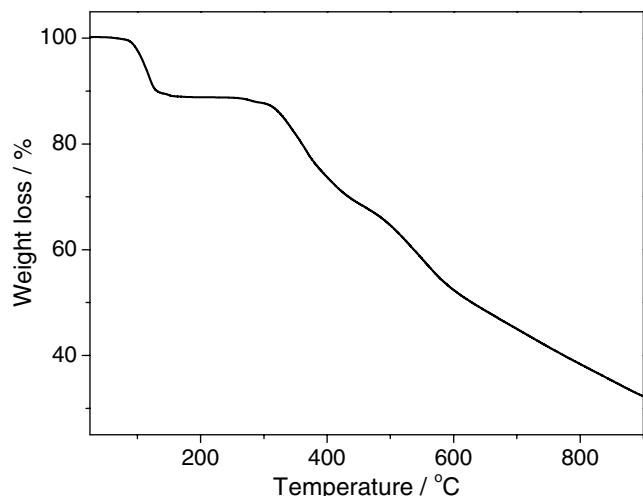


Fig. 1. TG curve of the $[\text{Tb}(\text{PHTHGLY})(\text{CBGLY})(\text{H}_2\text{O})_2](\text{H}_2\text{O})_3$ complex under a N_2 atmosphere and using heating rate of 10 °C/min.

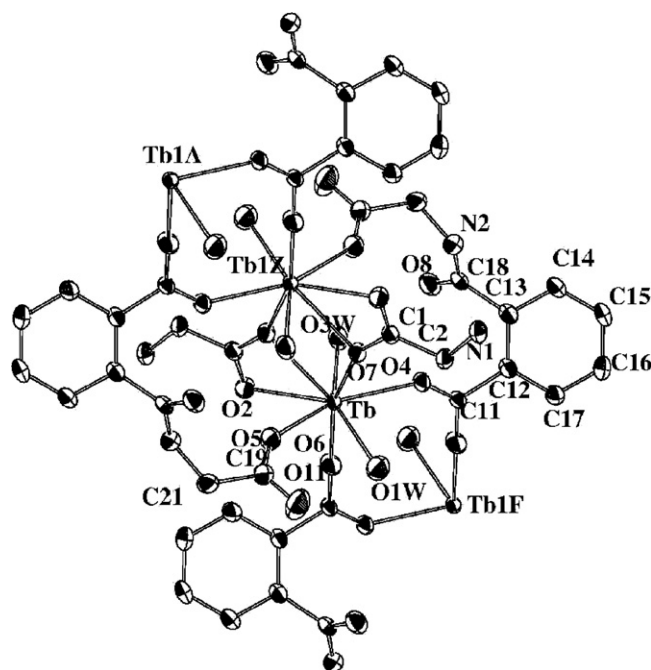


Table 1
Selected hydrogen-bonding in [Tb(PHTHGLY)(CBGLY)(H₂O)₂](H₂O)₃ complex

Hydrogen bond	d_{D-H} (Å)	$d_{A...H}$ (Å)	$d_{A...D}$ (Å)	$\angle D-H...A$ (°)
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

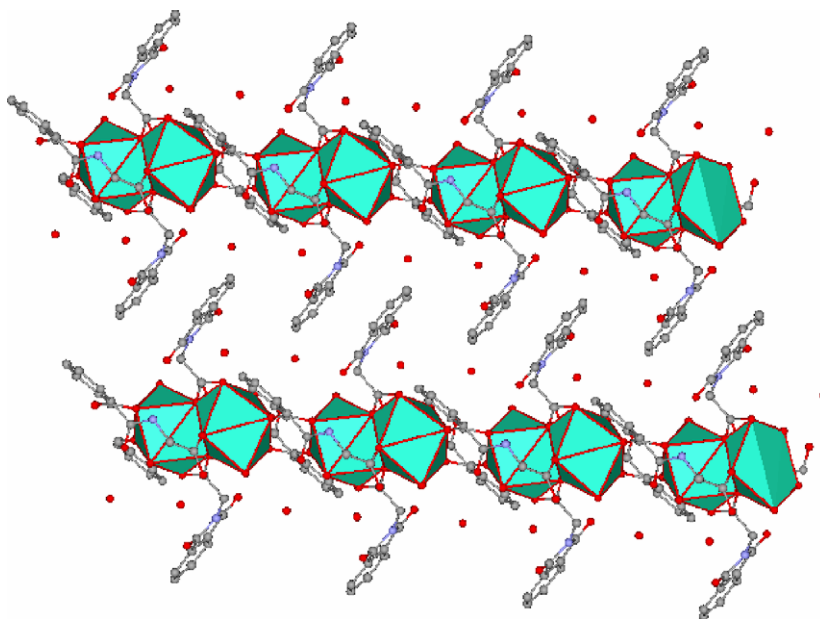


Fig. 4. Polyhedral representation of [Tb(PHTHGLY)(CBGLY)(H₂O)₂](H₂O)₃ complex. Green polyhedra are [TbO₈] unit, which are connected through carboxylate ligands. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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 ⁵D₄ → ⁷F₅ 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 S₀ → S₁ transitions of the PHTHGLY and CBGLY ligands. It is also observed narrow bands arising from 4f–4f transitions from the ground state ⁷F₆ level (nm) to the ⁵L₁₀(369), ⁵G₆(376), ⁵D₃(388) and ⁵D₄(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 Tb³⁺-complex in the solid state at liquid nitrogen temperature is shown in Fig. 5b. This spectrum displays characteristic narrow emission bands assigned to the ⁵D₄ → ⁷F_J transitions ($J=0, 1, 2,$

3, 4, 5 and 6), presenting the hypersensitive ⁵D₄ → ⁷F₅ transition as the most prominent which is extremely sensitive to chemical environment around Tb³⁺ 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 Tb³⁺ 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(π, π^*) of the ligands to the excited energy levels of the Tb³⁺ ion. The same behavior was observed for other Tb³⁺-carboxylate complexes [11].

In summary, our study demonstrated that the Tb³⁺ ion forms a new unexpected compound with two different carboxylate 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 Tb³⁺ ion. Additionally, the synthesized complex can activate efficiently the luminescence of Tb³⁺ ions by the substitution of two water molecules

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 $\{[\text{Tb}(\text{PHTHGLY})(\text{CBGLY})(\text{H}_2\text{O})_2](\text{H}_2\text{O})_3\}_\infty$ complex: Diffraction data of $[\text{Tb}(\text{PHTHGLY})(\text{CBGLY})(\text{H}_2\text{O})_2](\text{H}_2\text{O})_3$ complex were collected at room temperature with an Enraf-Nonius CAD4 Mach3 single crystal diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) 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 $[\text{Tb}(\text{PHTHGLY})(\text{CBGLY})(\text{H}_2\text{O})_2](\text{H}_2\text{O})_3$ complex was solved by Patterson method. Full-matrix least-squares refinement (on F^2) 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 $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_{15}\text{Tb}$ were, chemical_formula_weight = 658.32, $P\bar{1}$, unit cell parameters: $a = 9.079(9) \text{ \AA}$, $b = 10.186(6) \text{ \AA}$, $c = 14.673(6) \text{ \AA}$, $\alpha = 109.15(8)^\circ$, $\beta = 94.39(5)^\circ$, $\gamma = 106.36(9)^\circ$, $V = 1208.4 \text{ \AA}^3$, $Z = 2$, measurement temperature = 293(2), $D_c = 1.809 \text{ Mg m}^{-3}$, $\mu = 2.997 \text{ mm}^{-1}$, $F(000) = 652$. θ Range data collection 2.24–25.60. Reflections collected were obtained from a total of 4845 and independent/observed is 4540 ($R_{\text{int}} = 0.0212$) 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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