



Hydrothermal synthesis, crystal structure and physical properties of $\{[\text{Gd}(\text{H}_2\text{O})_4(\mu_2\text{-C}_6\text{NO}_2\text{H}_5)_2\text{Gd}(\text{H}_2\text{O})_4](\mu_3\text{-C}_6\text{NO}_2\text{H}_4)_2(\text{ZnCl}_3)_2\} \cdot 2\text{H}_2\text{O} \cdot 2\text{Cl}$

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ABSTRACT

A bimetallic 4f–3d tetranuclear complex $\{[\text{Gd}(\text{H}_2\text{O})_4(\mu_2\text{-C}_6\text{NO}_2\text{H}_5)_2\text{Gd}(\text{H}_2\text{O})_4](\mu_3\text{-C}_6\text{NO}_2\text{H}_4)_2(\text{ZnCl}_3)_2\} \cdot 2\text{H}_2\text{O} \cdot 2\text{Cl}$ (**1**) has been synthesized via hydrothermal reaction and structurally characterized by single-crystal X-ray diffraction. Complex **1** is characterized by a tetranuclear Gd_2Zn_2 structure with the gadolinium and zinc atoms interconnected by isonicotinic acid ligands. The tetranuclear species of $\{[\text{Gd}(\text{H}_2\text{O})_4(\mu_2\text{-C}_6\text{NO}_2\text{H}_5)_2\text{Gd}(\text{H}_2\text{O})_4](\mu_3\text{-C}_6\text{NO}_2\text{H}_4)_2(\text{ZnCl}_3)_2\}$ link to isolated chlorine ions and water molecules via $\pi \cdots \pi$ interactions and hydrogen bonds to yield a 3-D supramolecular framework. Photoluminescent investigation reveals that the title complex displays an emission in ultraviolet region. The solid-state diffuse reflectance spectra of **1** reveal the presence of a sharp optical gap of 3.66 eV.

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Trivalent lanthanide complexes continue to attract many researchers for several decades, the reason for that is probably due to the outstanding physical properties of these complexes and their applications as zeolite-like materials, catalysis, magnetic materials, electroluminescent devices as well as luminescent probes or labels in biological systems [1]. Furthermore, as for the numerous inorganic–organic (I–O) hybrid materials, the intriguing varieties of their topologies and architectures that can be obtained by self-assembling metal ions and multifunctional ligands also fascinate researchers. Nowadays, the syntheses of inorganic–organic hybrid materials based on transition metal ions have become pervasive [2], but there are relatively few documents on lanthanide I–O hybrid materials despite they can be used in luminescence and other fields [3]. Generally, lanthanide I–O hybrid materials with aromatic carboxylic acids as ligands show good thermal and luminescent stability for practical application. To our knowledge, group 12 (IIB) metal complexes are remarkably fascinating for many reasons like the variety of coordination numbers and motifs provided by the d^{10} configuration of the metal ions, the luminescence behaviors and the semiconductive properties. IIB elements (Zn, Cd and Hg) are very important for many semiconductor materials. It is proposed that complexes containing IIB elements should show some electric properties. Besides, isonicotinic anion is a very interesting species in forming extended structures because it is an unsymmetrical divergent ligand with a nitrogen atom at one side and two oxygen atoms from the carboxylato group at the other one. The isonicotinic anion can bridge two metal centers by bind-

ing to a metal center with the nitrogen atom and, to the other one, with one or two carboxylato oxygen atoms [4]. We propose that Ln–IIB (Ln = lanthanide) I–O hybrid materials with aromatic carboxylic acids as ligands maybe possess novel structural motifs and properties, such as luminescence, semiconductivity, catalysis, thermochromism and so on. Therefore, our group recently became interested in the crystal engineering of Ln–IIB I–O hybrid materials with isonicotinic acid as a ligand. We herein reported the synthesis, structure and properties of $\{[\text{Gd}(\text{H}_2\text{O})_4(\mu_2\text{-C}_6\text{NO}_2\text{H}_5)_2\text{Gd}(\text{H}_2\text{O})_4](\mu_3\text{-C}_6\text{NO}_2\text{H}_4)_2(\text{ZnCl}_3)_2\} \cdot 2\text{H}_2\text{O} \cdot 2\text{Cl}$ (**1**), which is the first tetranuclear Ln–TM (TM = transition metal) complex with isonicotinic acid as ligands.

Compound **1** was obtained from the reaction of $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, ZnCl_2 and isonicotinic acid by hydrothermal reaction [5]. X-ray diffraction analysis [6] reveals that the structure of the title complex consists of $\{[\text{Gd}(\text{H}_2\text{O})_4(\mu_2\text{-C}_6\text{NO}_2\text{H}_5)_2\text{Gd}(\text{H}_2\text{O})_4](\mu_3\text{-C}_6\text{NO}_2\text{H}_4)_2(\text{ZnCl}_3)_2\}^{2+}$ cationic moieties, Cl^- anions, and isolated water molecules, as shown in Fig. 1. The Zn1 atom is bound by three chlorine atoms and one nitrogen atom to form a ZnCl_3N tetrahedron. In ZnCl_3N tetrahedron, the bond lengths of Zn–Cl range from 2.231(1) to 2.2706(9) Å with an average value of 2.250(1) Å, which are normal and comparable with the counterparts found in the literature [7]. The gadolinium atom is coordinated by eight oxygen atoms, of which four are from four water molecules and four are from four isonicotinic acid ligands, yielding a distorted square anti-prism with the top and bottom planes defined by O(1W), O(2W), O(3W), O(4W) and O(1), O(3), O(2)($-x - 1/2, -y - 1/2, -z$), O(4)($-x - 1/2, -y - 1/2, -z$) atoms, respectively. The bond lengths of Gd–O_{isonicotinic acid} range from 2.334(2) to 2.374(2) Å with an average value of 2.350(2) Å, which is obviously shorter

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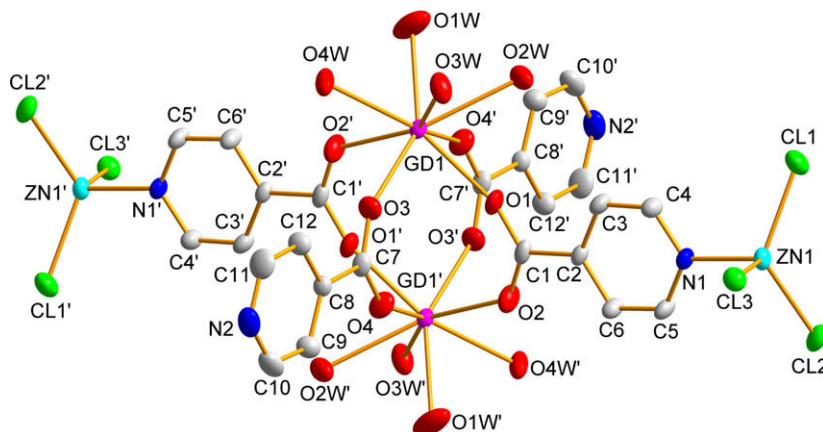


Fig. 1. ORTEP-drawing of **1** with 30% thermal ellipsoids. Lattice water molecules and isolated chlorine ions were omitted for clarity. Symmetry codes: ' $-x-1/2, -y-1/2, -z$.

than that of Gd–O_{water} being of 2.402(3)–2.523(3) Å, indicating that isonicotinic acid ligand has a stronger affinity to Gd^{III} ion than that of water. There are two crystallographic independent isonicotinic acid ligands that are grouped into two kinds, i.e. one acts as a bidentate ligand while the other acts as a tridentate ligand. The bidentate isonicotinic acid ligands should be protonated, as the case found in other Ref. [8]. To our knowledge, only several Ln–TM complexes containing both bidentate and tridentate isonicotinic acid ligands have been documented previously [9]. Two neighboring gadolinium atoms are bridged by two bidentate isonicotinic acid ligands to form a Gd₂ dimer with the Gd···Gd distance being of 4.4390(3) Å. The Gd₂ dimer is further bridged to two ZnCl₃ moieties via two tridentate isonicotinic acid ligands, yielding a tetranuclear $\{[\text{Gd}(\text{H}_2\text{O})_4(\mu_2\text{-C}_6\text{NO}_2\text{H}_5)_2\text{Gd}(\text{H}_2\text{O})_4](\mu_3\text{-C}_6\text{NO}_2\text{H}_4)_2(\text{ZnCl}_3)_2\}^{2+}$ cationic species. There are three kinds of hydrogen bonds in **1**, i.e. O···Cl, O···O and C···Cl hydrogen bonds, including O1W···O1W($-x, y, 1/2-z$), O4W···Cl1($1/2+x, 1/2+y, z$), O2W···Cl2($-1-x, -1-y, -z$), O3W···Cl2($-1-x, y, -1/2-z$), O3W···Cl3($-1-x, y, -1/2-z$), C11···Cl3($1/2+x, 1/2+y, z$), O1W···Cl4($x, -y, -1/2+z$), O2W···Cl4($-x, -y, 1-z$), and O4W···Cl4($-x, y-1, 1/2-z$) with the hydrogen bond distances

being of 2.908(7), 3.202(3), 3.153(3), 3.158(3), 3.127(3), 3.447(5), 3.075(4), 3.268(3), and 3.217(3) Å, respectively. In **1**, some $\pi\cdots\pi$ stacking interactions exist between two adjacent isonicotinic acid ligands located in two tetranuclear $\{[\text{Gd}(\text{H}_2\text{O})_4(\mu_2\text{-C}_6\text{NO}_2\text{H}_5)_2\text{Gd}(\text{H}_2\text{O})_4](\mu_3\text{-C}_6\text{NO}_2\text{H}_4)_2(\text{ZnCl}_3)_2\}^{2+}$ cationic species. The rings of the isonicotinic acid ligands involved in the $\pi\cdots\pi$ stacking interactions are arranged in such a way that the six atoms of the ring do not completely eclipse those of the other ring, meaning that the interaction is not “perfect face alignment” but “offset or slipped stacking”. For clarity, we define the pyridyl ring (containing N1 atom) of the isonicotinic acid ligand as R1. The R1 ring in an isonicotinic acid ligand has a $\pi\cdots\pi$ contact with a R1' ring in an adjacent isonicotinic acid ligand. The centroid to centroid distance is 3.688(2) Å for rings R1 and R1'. The perpendicular separation between R1 and R1' is ca. 3.635 Å. R1 slides from R1' by about 0.623 Å. The dihedral angle is 5.85° between R1 and R1'. The tetranuclear $\{[\text{Gd}(\text{H}_2\text{O})_4(\mu_2\text{-C}_6\text{NO}_2\text{H}_5)_2\text{Gd}(\text{H}_2\text{O})_4](\mu_3\text{-C}_6\text{NO}_2\text{H}_4)_2(\text{ZnCl}_3)_2\}^{2+}$ cationic species, the isolated chloride anions and the lattice water molecules are linked via hydrogen bonds and $\pi\cdots\pi$ stacking interactions to complete a 3-D supramolecular network, as shown in Fig. 2. Results of the bond valence calculations indicate that the gadolinium and zinc

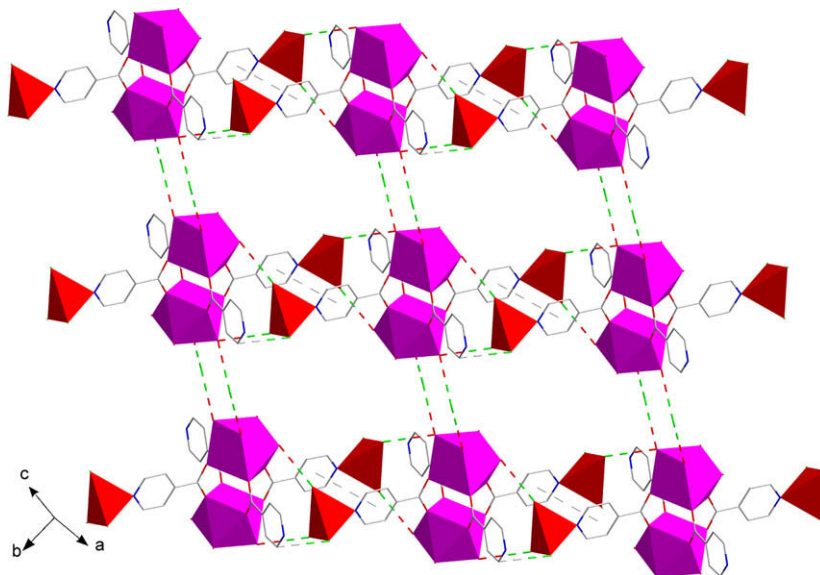


Fig. 2. Polyhedral perspective of **1** with the dashed lines representing $\pi\cdots\pi$ interactions and hydrogen bonds (Å): O1W···O1W($-x, y, 1/2-z$) 2.908(7), O4W···Cl1($1/2+x, 1/2+y, z$) 3.202(3), O2W···Cl2($-1-x, -1-y, -z$) 3.153(3), O3W···Cl2($-1-x, y, -1/2-z$) 3.158(3), O3W···Cl3($-1-x, y, -1/2-z$) 3.127(3), C11···Cl3($1/2+x, 1/2+y, z$) 3.447(5), O1W···Cl4($x, -y, -1/2+z$) 3.075(4), O2W···Cl4($-x, -y, 1-z$) 3.268(3), and O4W···Cl4($-x, y-1, 1/2-z$) 3.217(3).

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