

Short communication

## A novel heterometallic BaGa coordination polymer based on the bifunctional ligand 2,5-pyridine dicarboxylic acid

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## ABSTRACT

The first heterometallic BaGa coordination polymer (CP), namely  $[\text{Ba}_2\text{Ga}_2(\text{pydc})_4(\text{OH})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$  (**1**) ( $\text{H}_2\text{pydc}$  = 2,5-pyridine dicarboxylic acid), has been successfully synthesized by the reaction of the bifunctional ligand  $\text{H}_2\text{pydc}$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ga}_2\text{O}_3$  under hydrothermal conditions. Single-crystal X-ray diffraction analysis reveals that compound **1** features a three-dimensional (3D) network structure constructed from  $\text{Ga}_2(\text{OH})_2$  dimers incorporated Ba-pydc skeletons. Luminescence measurements showed that **1** exhibited strong emission band centered at 412 nm ascribed to the emission of ligand-to-ligand charge transfer, which was confirmed by theoretical studies.

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Heterometallic coordination polymers (CP) or metal-organic frameworks (MOFs) have gained increasing interest in recent years due to the possibly increased structural diversity and enhanced properties brought by the incorporation of different metal ions with distinct coordination ability and intrinsic properties [1–4]. To date, the 3d–4f heterometallic CPs have been well studied [5,6]. Yet relative less attention has been paid to that containing both p-block and alkaline-earth metal ions.

For the construction of heterometallic CPs, one of the key factors that must be considered is the different coordination abilities of the dissimilar metals [3], thus a bi- or multi-functional organic ligand or mixed ligands with different coordinating groups are preferred [7,8]. The Group 13 metal(III) ions are characteristic of easy hydrolysis of their salts during the synthetic process and smaller cation radii than that of rare earth element [9], which increase the difficulty of constructing heterometallic and even homometallic CPs based on the Group 13 metal(III) ions [10]. By contrast, the alkaline-earth Ba(II) with large cation radius is considered to be a structurally malleable metal ion in constructing the CPs with rich structural topology due to its high coordination number similar to that of lanthanide ions and strong affinity to O atom [11,12]. Thus the Ba(II) ion might be a good candidate in constructing heterometallic CPs based on Group 13 metal(III) ions.

Yet the heterometallic BaGa-CPs have not been documented. Thus far, there were only a few organometallic BaGa molecular complexes reported, such as  $[\text{Ba}\{\mu\text{-ddbfo}\}_2\text{GaMe}_2]_2$  (ddbfoH = 2,3-dihydro-2,2-dimethyl-7-benzofuranol) as single-source precursor for oxide materials

[13], and  $[\text{Ba}(\mu_4\text{-O})(\text{GaMe}_3)_2(\text{toluene})_2]_2$  obtained from homoleptic alkaline-earth metal silylamide complex [14]. In these molecular complexes, the organometallic Ga ligands act as Lewis acids to coordinate to the Ba with O and/or C donors.

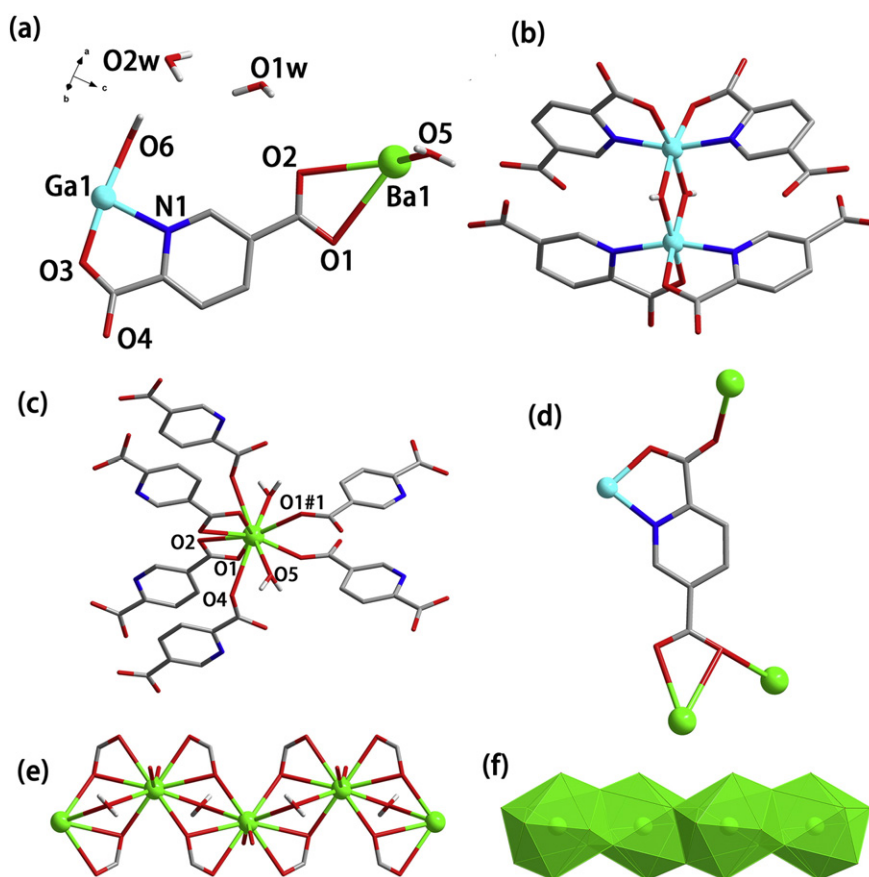
Herein, by choosing a bifunctional ligand 2,5-pyridine dicarboxylic acid ( $\text{H}_2\text{pydc}$ ), we have successfully obtained the first heterometallic BaGa-CP, namely  $\text{Ba}_2\text{Ga}_2(\text{pydc})_4(\text{H}_2\text{O})_2(\text{OH})_2 \cdot 3\text{H}_2\text{O}$  (**1**), via a hydrothermal reaction at 160 °C for 6 days [15]. Remarkably, the crystal was highly stable in air and common solvents conditions. The structure, thermal stabilities and luminescent properties of compound **1** have been studied in detail.

Compound **1** was obtained as light-yellow block-shaped crystals. Single-crystal X-ray diffraction analysis revealed that **1** crystallizes in the orthorhombic space group of *Fddd* [16]. As shown in Fig. 1a, the asymmetric unit contains a quarter of the formula unit, that is, half a crystallographically independent Ba(II) ion, half a Ga(III), one fully deprotonated pydc ligand, half a coordinated water molecule, half a  $\text{OH}^-$ , and 0.75 guest water molecule, Fig. 1a. The existence of Ba and Ga in **1** was confirmed by EDX (Fig. S1, ESI). As illustrated in Fig. 1b, each Ga(III) is six-coordinated as by two chelating pydc ligands with a N (N1) and an O (O3) donor of *o*- $\text{COO}^-$  and two OH groups (O6) to afford a distorted octahedron; then two OH groups bridge two such Ga atoms to form a dimeric  $[\text{Ga}_2(\text{pydc})_4(\text{OH})_2]$ . The Ga–O—bond lengths range from 1.934 (4) to 1.969 (4) Å, and the Ga–N—bond length is 2.083 (3) Å, which are in the average range of Ga–O/N bond lengths [17].

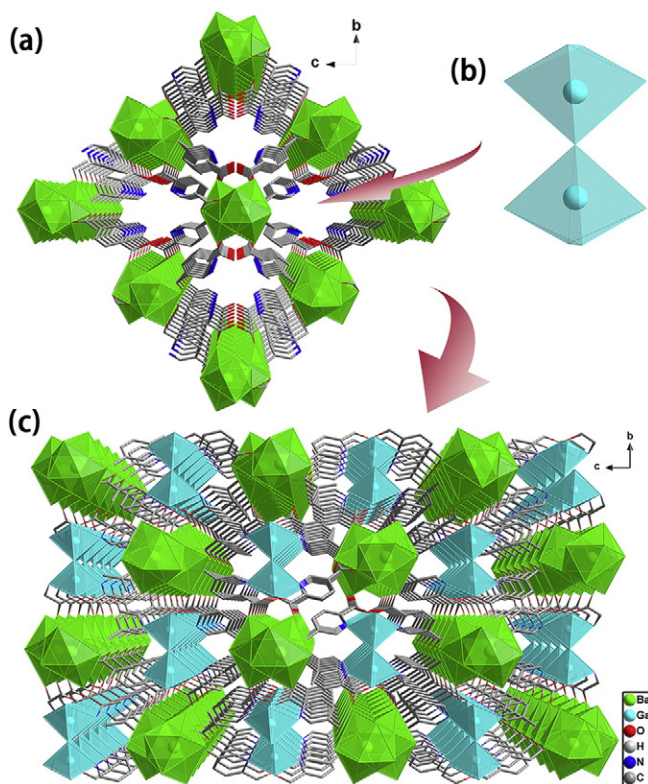
Each Ba(II) ion is coordinated to ten oxygen atoms from six carboxylate groups of six different pydc ligands and two bridging  $\text{H}_2\text{O}$  molecules to generate a dicapped-dodecahedron coordination geometry,

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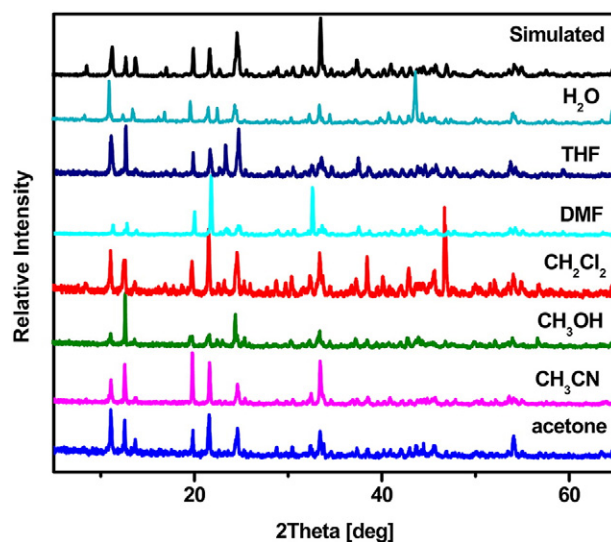
**Fig. 1.** (a) Asymmetric unit of compound **1**; (b) the dimeric  $[\text{Ga}_2(\text{pydc})_4(\text{OH})_2]$  in compound **1**; (c) the coordination of Ba ion in compound **1**; (d) the coordination mode of ligand pydc in **1**; (e) the  $[-\text{Ba}-(\text{COO})_2(\text{H}_2\text{O})-\text{Ba}-]_n$  chain; (f) the polyhedral view of the  $[-\text{Ba}-(\text{COO})_2(\text{H}_2\text{O})-\text{Ba}-]_n$  chain.



**Fig. 2.** (a) The 3D Ba-pydc framework in compound **1** viewed along the  $a$  axis; (b) polyhedral view of the  $[\text{Ga}_2(\text{OH})_2]$  dimer; (c) the framework of **1** viewed along the  $a$  axis.

Fig. 1c. Furthermore, the  $[\text{BaO}_{10}]$  polyhedra share faces with each other generating an infinite  $[-\text{Ba}-(\text{COO})_2(\text{H}_2\text{O})-\text{Ba}-]_n$  chain along the crystallographic  $b$  axis (Fig. 1e and f). The Ba—O distances range from 2.730 (3) to 3.0004 (4) Å (Table S2), which are comparable to that of reported Ba(II) ions [18–20].

As shown in Fig. 1d, the ligand pydc only shows one coordination mode. Its pyridine N and O atom of the  $o$ -COO<sup>−</sup> group chelate to a Ga atom; the remaining O atom of the  $o$ -COO<sup>−</sup> group monodentates to a



**Fig. 3.** The powder X-ray diffraction patterns of compound **1** after immersed in different solvents for two days and in  $\text{H}_2\text{O}$  for one week.

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