

Short communication

The roles of H-bonding, π-stacking, and antiparallel CO···CO interactions in the formation of a new Gd(III) coordination polymer based on pyridine-2,6-dicarboxylic acid

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ABSTRACT

This study reports the synthesis of a new catenane Gd(III) complex using pyridine-2,6-dicarboxylic acid ($H_2\text{pydc}$) as ligand. The structure of $[\text{Gd}(\text{pydc})(\text{Hpydc})(\text{H}_2\text{O})_2]_n$ (**1**) was characterized by IR spectroscopy, X-ray diffraction methods and the elemental analysis to check the purity of the compound. On the basis of crystallographic data, compound **1** contains a Gd(III) metal center that is coordinated to seven oxygen atoms of two tridentate and one monodentate $H_2\text{pydc}$ ligands and two coordinated water molecules. Other lanthanoid complexes involving this ligand are available in the literature; however, this is the first example where a combination of monoanionic (Hpydc^-) and dianionic (pydc^{2-}) forms of the ligand counterbalance the Gd^{3+} metal center. The intermolecular interactions in this novel system consist of different kinds of H-bonding and π -stacking interactions in addition to antiparallel CO···CO interactions which have been analyzed using DFT calculations and the Bader's theory of "atoms in molecules".

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Studies on the complex formation of metal ions with pyridine-2,6-dicarboxylic acid ($H_2\text{pydc}$) as a ligand are abundant in the literature because of its ability for giving different coordination modes as well as stable chelates through two carboxylate groups that may be completely or partially deprotonated and the nitrogen of the pyridine ring [1]. In addition to the high coordination ability of $H_2\text{pydc}$, it shows an interesting capacity to form a variety of supramolecular assemblies in the solid state dominated by directional interactions of the metal-pydc unit with the other moieties including classical and non-classical hydrogen bonds [2] and π -stacking interactions [3,4].

There are several works in the literature where Gd^{3+} networks have been reported and the supramolecular interactions have been analyzed [5–7]. Herein we report the synthesis and X-ray characterization of a new catenane Gd(III) complex using pyridine-2,6-dicarboxylic acid as ligand. The structure of $[\text{Gd}(\text{pydc})(\text{Hpydc})(\text{H}_2\text{O})_2]_n$ (**1**) was characterized by different spectroscopic methods and some noncovalent interactions have been studied using DFT calculations combined with the Bader's theory of "atoms in molecules" [8].

The synthetic procedure and spectroscopic characterization of compound **1** are given in the supporting information. The structure consists of chains of metal complexes with bridging pydc ligands which extend

parallel to the *c* axis (Fig. 1). The geometry around Gd is a distorted mono-capped square antiprism. Two set of atoms *i.e.* O1, O3, O6, O8 and O5, O7, O10, N2 construct the frontier planes and N1 is the cap. Two boundary planes are nearly parallel with the angle between them only 3.06°. The average bond lengths of $\text{Gd}-\text{O}_{\text{crx}}$ and $\text{Gd}-\text{OW}$ are 2.46 and 2.39 Å, respectively showing that the metal-water bonds are stronger. The Gd complexes are joined together by O7 bridges to generate 1D polymers along the *c* axis (Fig. 2). Details of the crystal structure solution are summarized in Table S1 and selected bond lengths and angles are listed in Table S2.

The O6-H6B···O8 hydrogen bond (1.964 Å and 147.2°) forms an $S_1^1(6)$ [9] synthon which leads to greater stability of the system. Additionally, 1D polymers extend along the *b* axis through the hydrogen bond interactions with water molecules (OW13, OW14). Finally, polymers (see Fig. 3) are generated along the *a* axis by hydrogen bonds involving water molecules OW11 and OW12 between polymers as well as π - π interactions (Cg: C9 C10 C11 C12 C13 N1, 4.211 Å) (see Fig. 3a). In addition, the –COOH groups of the organic ligand also establish H-bonding interactions with water molecules (see Fig. 3c). Moreover, in Fig. S2 we provide a close-up view and geometric details of the zig-zag chain of the four lattice water molecules seen between the rows of complexes in Fig. 3.

The theoretical study is devoted to analyzing the antiparallel CO···CO interactions [10] observed in the solid state of **1**. Fig. 4a shows a fragment of the packing in compound **1** where the formation

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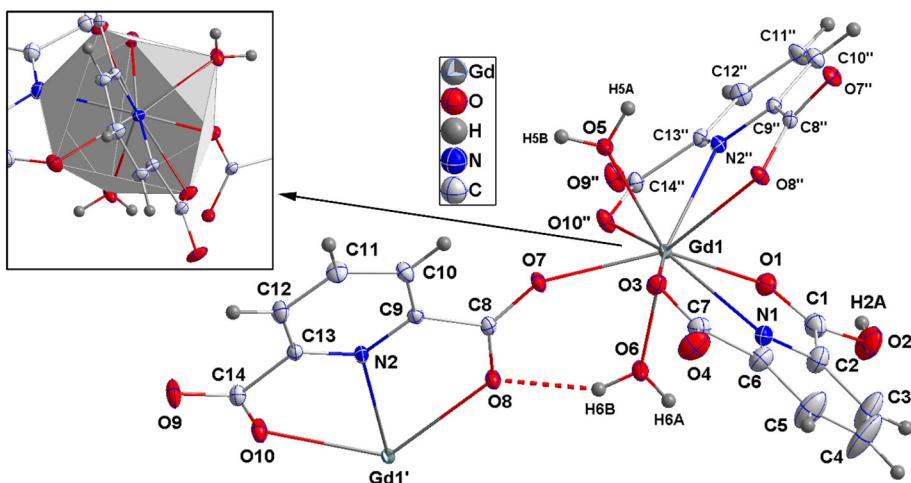


Fig. 1. View of the generator of the chain structure with labeling scheme ('atoms are at $x, 3/2 - y, 1/2 + z$ and the "atoms are at $x, 3/2 - y, -1/2 + z$).

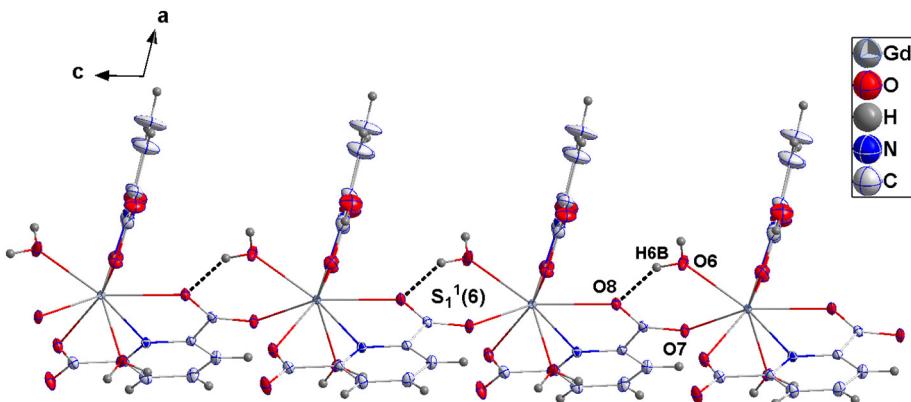


Fig. 2. 1D polymeric structure of **1** along the *c* axis.

of this interaction is highlighted. The infinite 1D chains are interconnected by antiparallel CO···CO interactions that are established between the coordinated carboxylate and carboxylic groups of the ligands belonging to two different chains. These interactions along with the H-bonding interactions involving the water molecules as indicated

above (see Fig. S2) are responsible for the formation of the 2D layers. To evaluate this interaction energetically, we have used a theoretical model retrieved from the crystallographic coordinates (see Fig. 4b) where one monodentate ligand has been replaced by a water molecule. Using this model, the complex remains neutral (coordinated to Hpydc⁻

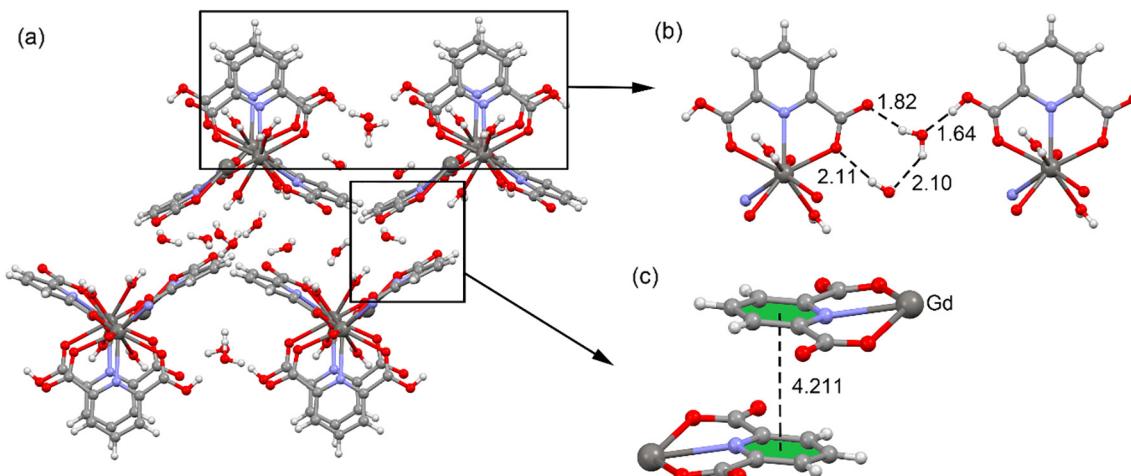


Fig. 3. (a) X-ray solid state structure of **1** in the *ab* plane. (b) H-bonding involving the COOH group. (c) Detail of the π - π interaction. Distances in Å.

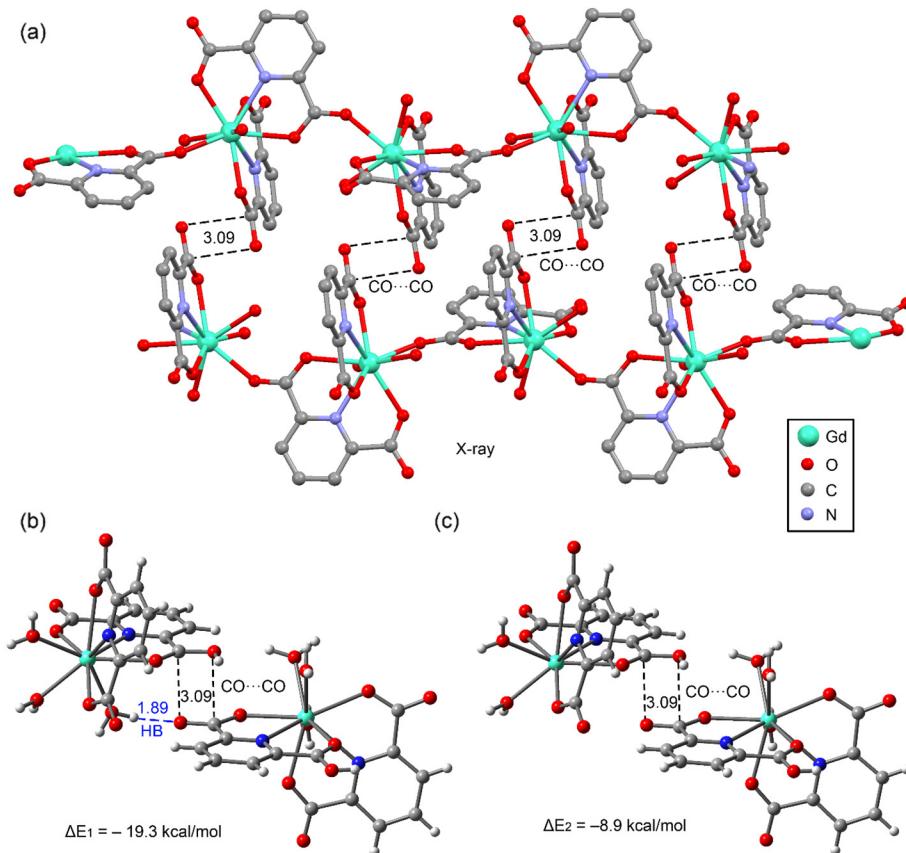


Fig. 4. (a) X-ray fragment of **1**. (b, c) Theoretical models used to evaluate the CO···CO interactions. Distances in Å. Gd atom is represented in light blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and pydc²⁻) and each polymeric chain is reduced to a monomer. Therefore, this supramolecular system can be used as a minimalist model for the antiparallel CO···CO interaction of the polymeric chains. It should be emphasized that this dipole-dipole interaction involves a carbonyl of one coordinated carboxylate group and the hydroxyl of the other coordinated carboxylic group. To our knowledge, this type of interaction has not been described before. We have computed the formation energy of this assembly (dimer) which is large and negative $\Delta E_2 = -19.3$ kcal/mol, thus confirming its importance in the formation of the 2D layer. It can be observed that a hydrogen bond involving the coordinated water molecule and the carboxylate group (blue dashed line in Fig. 4b) is also involved in the formation of this dimer. In an effort to evaluate the contribution of the CO···CO interaction we have used another theoretical model where this coordinated water molecule has been eliminated (see Fig. 4c). As a result, the interaction energy is reduced to $\Delta E_2 = -8.9$ kcal/mol, that is the contribution of the antiparallel CO···CO interaction and the difference with ΔE_1 (-10.4 kcal/mol) is the contribution of the H-bond. The CO···CO interactions have been also characterized using the Bader's theory of "atoms in molecules" (AIM), see ESI and Fig. S3.

In the present study we have synthesized and X-ray characterized a new Gd(III) coordination complex using pyridine-2,6-dicarboxylic acid as ligand. We have described the importance of unconventional CO···CO interactions involving the coordinated carboxylate and carboxylic groups in the solid state of both compound **1**. It likely plays a key role in the formation of 2D layers connecting the 1D polymeric chains. The energetic feature of this interaction has been studied by means of DFT calculations and characterized using the Bader's theory of atoms in molecules.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.inoche.2017.05.029>.

References

- [1] H. Eshagh-Hosseini, H. Aghabozorg, M. Mirzaei, M.M. Amini, Y.-G. Chen, A. Shokrollahi, R. Aghaei, *J. Mol. Struct.* 973 (2010) 180.
- [2] (a) G.R. Desiraju, *Chem. Commun.* (2005) 2995;
(b) G.R. Desiraju, *Acc. Chem. Res.* 29 (1996) 441.
- [3] C. Janiak, *J. Chem. Soc. Dalton Trans.* 21 (2000) 3885.
- [4] M. Mirzaei, H. Aghabozorg, H. Eshagh-Hosseini, *J. Iran. Chem. Soc.* 8 (2011) 580.
- [5] G. Makhloufi, B. Francis1, J. Dechnik, A. Strzelczyk, C. Janiak, *Polyhedron* 127 (2017) 59–67.
- [6] B. Gil-Hernández, J.K. Maclarens, H.A. Höpke, J. Pasán, J. Sanchiz, C. Janiak, *CrystEngComm* 14 (2012) 2635–2644.
- [7] B. Gil-Hernández, H.A. Höpke, J.K. Vieth, J. Sanchiz, C. Janiak, *Chem. Commun.* 46 (2010) 8270–8272.
- [8] R.F.W. Bader, *Atoms in Molecules - A Quantum Theory*, Oxford University Press, Oxford, U.K., 1990
- [9] M.C. Etter, J.C. MacDonald, J. Bernstein, *Acta Crystallogr. B* 46 (1990) 256–262.
- [10] R. Prohens, A. Portell, M. Font-Bardia, A. Bauzá, A. Frontera, *CrystEngComm* 18 (2016) 6437.