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Isonicotinohydrazide conformation in a supramolecular system with 1,4-benzenedicarboxylic acid and Zn^{2+} and Mn^{2+}

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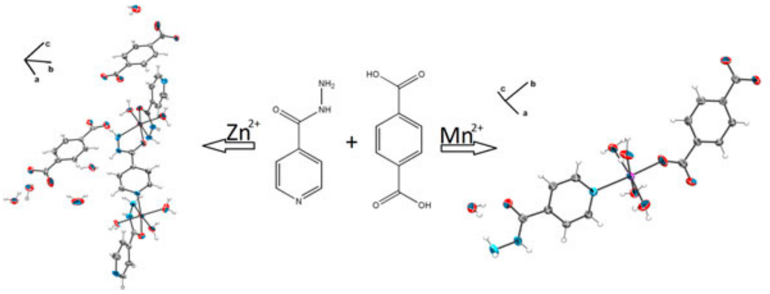

An anti-tuberculosis drug, isonicotinohydrazide (INH), is studied concerning its conformation in different crystalline environments. In the present work, compounds with zinc (**1**) and manganese (**2**) ions are reported where INH has different conformations, caused by hydrogen bonds with 1,4-benzenedicarboxylic acid (H_2BDC) and water molecules and by coordination bonds involving its functional groups. In **1**, INH is coordinated to two zinc ions, where H_2BDC and crystallization water molecules form several hydrogen bonds giving rise to a complex three-dimensional (3-D) network. In **2**, both INH and H_2BDC molecules are coordinated to manganese as well as four water molecules. The complex formed interacts by hydrogen bonds forming a 2-D arrangement. A 3-D network extension arises from other hydrogen bonds generated by crystallization water. In these two compounds, the presence of BDC ion and water molecules is very important in the stabilization of the complexes and in INH conformation. This work is focused on the structural description of formed compounds.

Keywords: Hydrogen bonds; Twining structure; Isonicotinohydrazide

1. Introduction

In supramolecular chemistry, the study of drug molecules is important to provide a good understanding among their properties and intermolecular interactions [1–5]. The objective in this work is to study isonicotinohydrazide (INH) [figure 1(a)]. This compound was first

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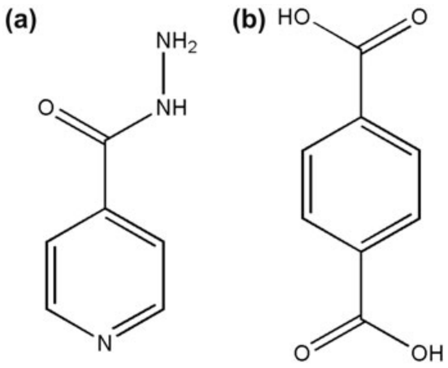


Figure 1. Molecular structure of (a) INH and (b) H_2BDC.

reported in 1952, and it is a potent agent in tuberculosis treatment [6]; its crystalline structure is already reported and this molecule is well known [7, 8].

In the solid state, INH molecules form specific hydrogen bonds, composed by interactions between hydrazide and pyridine groups through N–H···N interactions [8]. There are also some reported structures with INH coordinated to transition metal ions [9–12]; the hydrogen bond networks are different to those observed in the INH structure, mainly due to coordination and the presence of counter ions which contain acceptor atoms for hydrogen bonds, like ClO_4, and/or water molecules in the structure. Another difference occurs because the nitrogen of pyridine is coordinated and does not form hydrogen bonds like in free INH. Similarly, interactions involving coordinated hydrazide groups are quite different in geometrical parameters, like distances and angles. These differences influence coordination environment, different counter ions or solvents that are involved in solid-state stability. Investigation about how these hydrogen bonds differ and how it can change the INH conformation is very interesting. For example, when INH forms complexes with copper, its conformation does not change significantly [9, 10]. In one of these compounds, the coordination occurs only through the hydrazide group and the metal site forms a roughly square planar geometry [9]. In the other one, INH coordinates also by pyridine forming a distorted tetrahedral coordination geometry [10]. When INH coordinates to zinc [11], both hydrazide and pyridine groups are coordinated, changing the INH conformation. This change is related to the angle between hydrazide and pyridine group which may increase with a decrease in zinc–zinc distance [11] coordinated at both groups. The zinc ion presents a distorted octahedral geometry; this geometry will also be expected in the compound formed and described in this work.

This study will focus on a structural study of coordination of INH with zinc and manganese ions, combined with the 1,4-benzenedicarboxylic acid (H_2BDC), which is displayed in figure 1(b). H_2BDC is a divergent and rigid ligand and its complexation with metal ions is well described in the literature [13–15].

Addition of H_2BDC in the system may favor the formation of new intermolecular interactions, by carboxylic groups or aromatic rings with INH functional groups and solvents, contributing to stabilization and crystallization of the supramolecular system. These interactions as well as the presence of a metallic ion and solvents can provide INH molecules with different conformations that give different properties to the system. These different conformations and interactions that influence properties will be the focus of this work.

2. Experimental

All chemicals were purchased by Aldrich® and used without purification. The syntheses with INH, H_2BDC, and metal ions (zinc and manganese) are described below.

The basic characterization and its instrumental parameters were: elemental analyses (CHN) were performed on a Perkin-Elmer 2400 analyzer. Infrared spectroscopy was performed on a FT-IR spectrometer (Bomen MB102) from 4000 to 400 cm^{-1} with an average of 64 scans and 4 cm^{-1} spectral resolution using KBr pellets as sample support. Raman spectroscopy was performed on a Bruker RFC 100 instrument equipped with an Nd^{3+}/YAG laser operating at 1064 nm in the near infrared and a CCD detector cooled with liquid nitrogen, averaging 200 scans with 4 cm^{-1} of spectral resolution. Thermogravimetric analysis (TGA) and its derivative (DrTGA) were performed on a Shimadzu DTG60 instrument with a heating rate of 10 °C min^{-1} under N_2.

2.1. *Synthesis of $Zn_2C_{34}H_{49}N_6O_{21}$ (1)*

This compound was synthesized using solvothermal methodology. The ligands were added in a beaker, 0.05 g (0.36 mM) of INH, 0.0605 g (0.36 mM) of H_2BDC, 0.029 g (0.72 mM) of NaOH, and 0.1357 g (0.36 mM) of $Zn(ClO_4)_2{\cdot}6H_2O$. All ligands were mixed and transferred using 30 mL of water as a solvent to an autoclave. After this procedure, the mixture was heated to 120 °C and maintained for 50 hours. At the end of the syntheses, no precipitated product was formed, but all ligands were solubilized. The solution was placed at rest for three months. After this time, a single dark yellow crystal with two centimeter length was formed. This crystal was separated and sliced to be characterized and submitted for single-crystal X-ray diffraction. *Elemental analyses*: Calcd for $Zn_2C_{34}H_{49}N_6O_{21}$ (%): C, 38.87; H, 4.10; N, 12.00. Found (%): C, 38.93; H, 4.71; N, 11.89. IR (KBr, cm^{-1}): $3233_{m}(\nu_{NH_2})$, $1641_{vw}(NH_{2scissoring})$, $1604_{m}(\nu_{asym(COO)^-})$, $1551_{m}(\nu_{CC/CN})$, $1419_{sh}(\nu_{C=C}+\delta_{C=C-C})$, $1388_{s}(\nu_{sym(COO)^-})$, $1017_{w}(\nu_{py}+\delta_{py})$. Raman ($cm^{-1}$): $3078_{m}(\nu_{CH})$, $1669_{vw}(\nu_{CO})$, $1611_{s}(\nu_{py}+\delta_{CH})$, $1551_{w}(\nu_{CC/CN})$, $1399_{m}(\nu_{sym(COO)^-})$, $1004_{w}(\nu_{py})$.

2.2. *Synthesis of $MnC_{14}H_{21}N_3O_{10}$ (2)*

This compound was synthesized by simple mixture. In the same beaker, 0.05 g (0.36 mM) of INH, 0.0605 g (0.36 mM) of H_2BDC, and 0.029 g (0.72 mM) of NaOH were added. After this, 20 mL of water was added and the mixture was heated at 100 °C and stirred until that all dissolved. In another beaker, 0.0925 g (0.36 mM) of $Mn(ClO_4)_2{\cdot}6H_2O$ in water was added.

When both solutions were 25 °C, the solution with $Mn(ClO_4)_2{\cdot}6H_2O$ was added slowly, with stirring, in the solution with INH and H_2BDC. Then, this mixture was carried to the refrigerator. After 24 h, the formation of colorless crystals was observed and they were separated to be characterized. *Elemental analyses*: Calcd for $MnC_{14}H_{21}N_3O_{10}$ (%): C, 37.68; H, 4.74; N, 9.42. Found (%): C, 37.85; H, 4.66; N, 9.52. IR (KBr, cm^{-1}): 3339_{w} (ν_{NH}), $1644_{w}(NH_{2scissoring})$, $1563_{s}(\nu_{asym(COO)^-})$, $1419_{sh}(\nu_{C=C}+\delta_{C=C-C})$, $1377_{s}(\nu_{sym(COO)^-})$, $1017_{m}(\nu_{py}+\delta_{py})$. Raman ($cm^{-1}$): $3080_{m}(\nu_{CH})$, $1646_{w}(NH_{2scissoring})$, $1611_{s}(\nu_{py}+\delta_{CH})$, $1550_{w}(\nu_{CC/CN})$, $1343_{m}(\nu_{sym(COO)^-})$, $1012_{m}(\nu_{py})$.

2.3. *Single-crystal X-ray diffraction*

The single-crystal X-ray diffraction measurements were performed with an Oxford Gemini A Ultra-radiation instrument with a CCD detector using MoKα radiation ($\alpha = 0.71073$ Å) at room temperature. The data collection, reduction, unit-cell refinement, and absorption correction were performed using CrysAlis RED software (Oxford Diffraction Ltd, version 1.171.35.15) [16]. The structures were solved and refined using SHELX-97 [17], and the figures were produced by Ortep 3 for Windows [18], Mercury [19], Pov-Ray [20], and Vesta [21].

3. Results and discussion

The synthesis procedure described for **1** was also tried with manganese ion as well as the synthetic method for **2** was also tried with zinc ion. However, no crystalline compound was obtained in this way. In solvothermal method, only Zn compound was obtained and by simple mixture synthesis, only formation of the Mn compound was observed.

The vibrational spectra are displayed in figure S1 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2015.1016007), as well as the TGA (figure S2). In table 1, the crystallographic data for diffracted single crystal of **1** are provided. The crystallographic data treatment of diffracted crystal was not trivial, because this sample was twinned. Non-merohedral twinning [22, 23], where each unit cell for each component does not coincide in some crystallographic axis [22, 23] was observed. Thereby, in the crystal data, two different components with same composition and unit cell were found, but with different orientations. A treatment using the CrysAlis RED software [15] allows us to separate these components and to reach a good twinning refinement. In this sense, 44.3% of

Table 1. Crystallographic data of **1** and **2**.

Formula	$Zn_2C_{34}H_{49}N_6O_{21}$ • **1**	$MnC_{14}H_{21}N_3O_{10}$ • **2**
Formula weight (g M^{-1})	1050.56	446.28
Crystal system	Triclinic	Monoclinic
Space group	*P1*	*P2$_1$*
a (Å)	7.5788(3)	6.5447(2)
b (Å)	11.4902(8)	21.2449(5)
c (Å)	13.0516(6)	7.0218(3)
α (°)	79.632(5)	90.0
β (°)	73.334(4)	90.0
γ (°)	79.799(5)	111.327(4)
V (Å^3)	1061.50(10)	909.46(5)
Z	1	2
D_{Calcd} (g cm^{-3})	1.643	1.63
Crystal size	0.725 × 0.592 × 0.452	0.810 × 0.161 × 0.105
μ (Mo Kα) (cm^{-1})	1.225	0.787
Measured reflection/unique	23,123/16,863	16,033/4453
Observed reflection [$F_o^2 > 2\sigma(F_o^2)$]	13,820	3827
Flack parameter	0.381(12)	−0.011(15)
Parameter number	596	297
R [$F_o > 2\sigma(F_o)$]	0.0634	0.0371
wR [$F_o^2 > 2\sigma(F_o)^2$]	0.1925	0.0781
S	1.034	1.092
RMS (e Å^{-3})	0.107	0.067

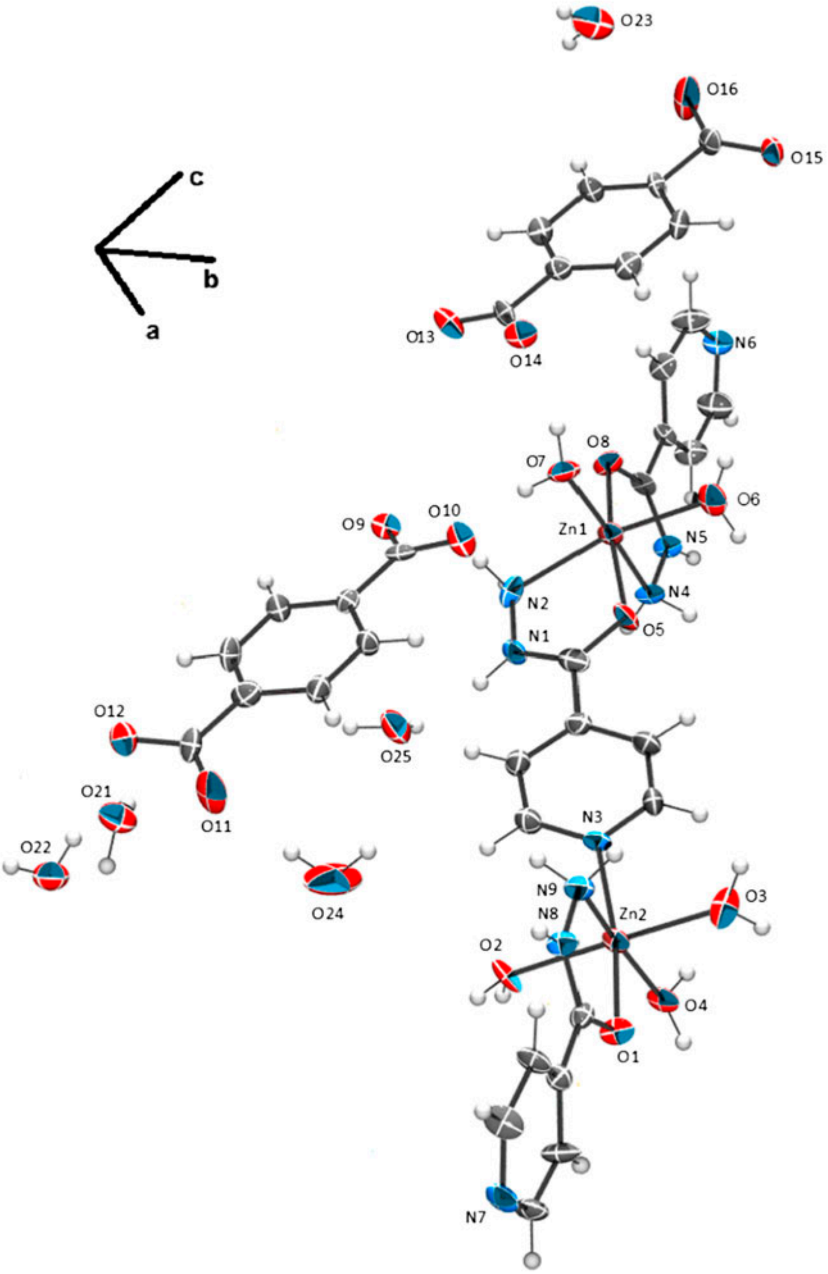


Figure 2. Asymmetric unit of **1**.

X-ray reflections were indexed as component one, 37.7% as component two, 17.8% as overlapping reflections belonging to both components, and 0.2% were non-indexed.

In figure 2, the asymmetric unit of refined structure of **1** is displayed. Analyzing the structure, it presents three molecules of INH, two BDC ions, two Zn^{2+}, and 10 waters, where five of them are crystallization molecules and the other five are coordinated. The complex is formed by three molecules of INH and five waters coordinated to two different zinc metallic centers, which are crystallographically independent. The quantity and type of water molecules were confirmed by TGA (figure S2). Zinc ions have a distorted octahedral geometry with different coordination spheres (figure S3). In order to facilitate the analysis, the INH in **1** will be termed INH1, INH2, and INH3 (scheme 1).

In **1**, several hydrogen bond interactions classified as medium to weak were observed. Here, we will highlight only the most important hydrogen bonds involved in crystal stabilization and structure conformation. BDC ion is involved in several hydrogen bonds with the complex (figure 3) by carboxylate that stabilize the solid state. The main interactions are O4–H4A···O9, O7–H7A···O10, O7–H7B···O14, O3–H3B···O14, and O4–H4B···O13 which present distances of 2.707(7), 2.645(8), 2.699(7), 2.774(7), and 2.664(8) Å, respectively, between donor and acceptor. These hydrogen bonds form two close paths (figure 3), one with O3–H3B···O14 and O4–H4B···O13 and the second with O4–H4A···O9, O7–H7A···O10, O7–H7B···O14, and O4–H4B···O13; with $R_2^2(8)R_4^4(12)$ graph set motif [24].

BDC forms important hydrogen bonds with crystallization water molecules. Figure 4(a) shows those interactions extending alternately between BDC and water. In this formation, there are three sets detached as hydrogen bonds: one, at red color [figure 4(a) and (b)], is formed by O21–H21B···O15, O21–H21A···O11, O22–H22B···O16, and O22–H22A···O12 and make a path that extends the structure in the diagonal of the unit cell (1 1 1), alternating with hydrogen bonds (black color) [figure 4(a) and (c)]. These interactions are those formed between BDC ion and coordination water, the second set in figure 3. The last set of

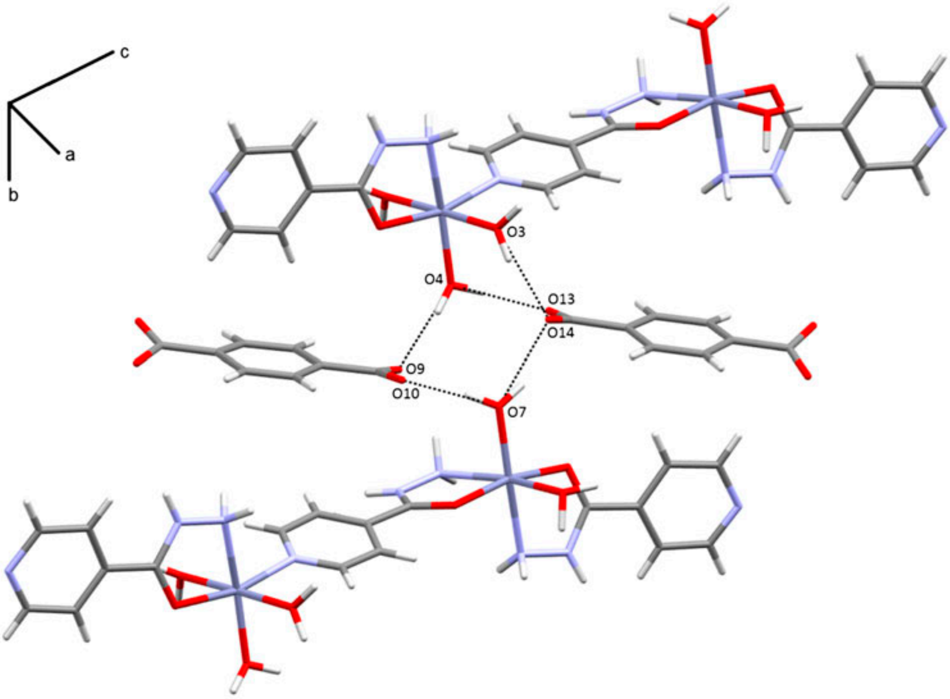


Figure 3. Hydrogen bonds formed with carboxylate groups of BDC in **1**.

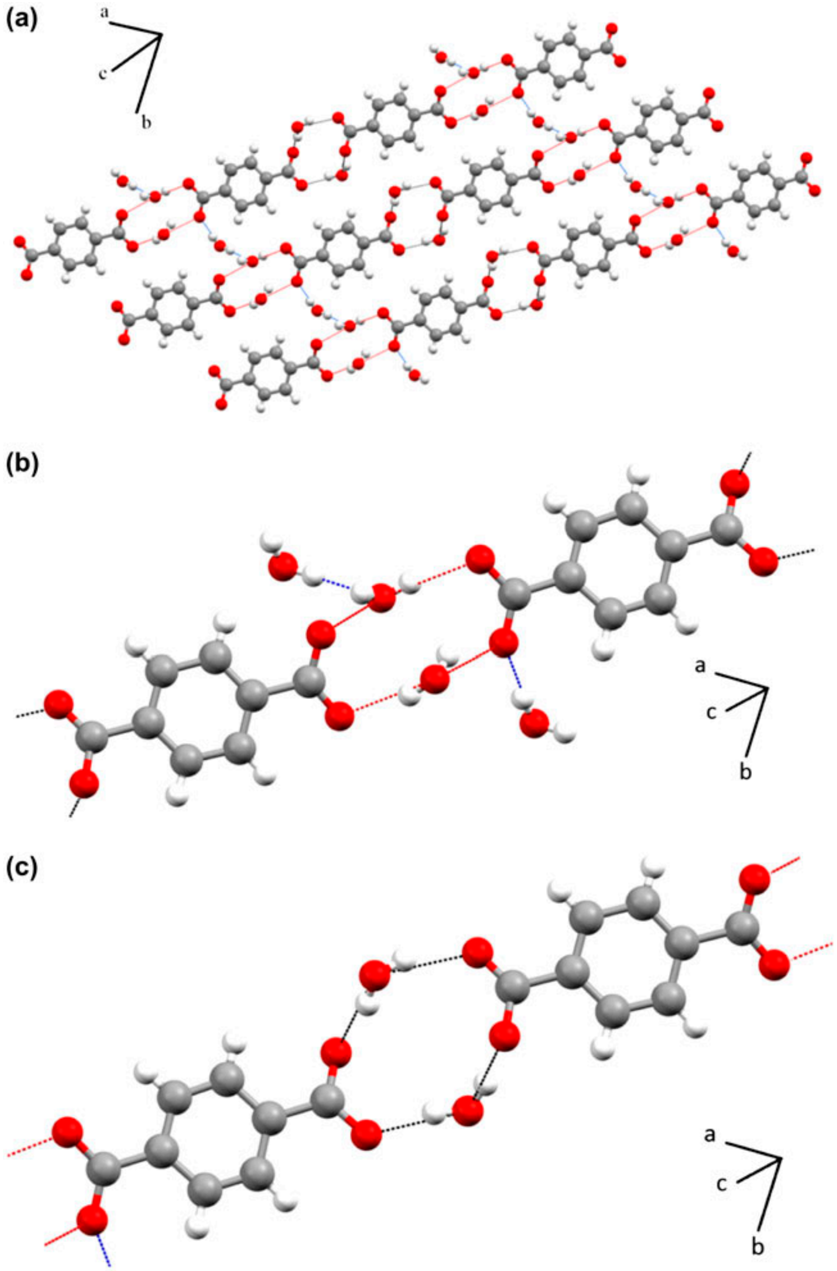


Figure 4. (a) The three sets of hydrogen bonds in **1** among BDC ions and water molecules, (b) red and blue sets, and (c) black set (see http://dx.doi.org/10.1080/00958972.2015.1016007 for color version).

hydrogen bonds is formed between O24–H24A···O22 and O24–H24B···O11 that is blue in color [figure 4(a) and (b)] and extends the crystalline arrangement in diagonal of *ac* plane (1 0 1). Alternately, with red hydrogen bonds, this combination forms a chain of hydrogen bonds with $C_3^3(8)R_4^4(12)$ graph set. These three sets extend and stabilize the structure in the 3-D crystalline space.

The angle formed between hydrazide group and pyridine ring in INH species has been reported [9, 10]. In neutral molecule, this angle is 18.1° and when INH is coordinated to two zinc ions, this angle is 37° or 45°, depending on the distance of zinc. In **1**, this angle in INH1 and in INH3 are very similar [17.4(2)° and 17.5(5)°, respectively], and they are relatively close to the neutral INH molecule. In this way, for INH1 and INH3, coordination does not interfere substantially in its conformation, and additionally, the bond lengths are also close to the neutral INH crystal structure [8, 9]. There are two kinds of hydrogen bonds that involve these hydrazide groups, one with BDC (N5–H5···O12 and N8–H8···O15) and another one with crystallization water (N4–H40B···O21 and N9–H9C···O22) that contribute to stabilize this conformation (figure S4).

Analyzing the conformation of INH2, there are some differences compared with free molecules. INH2 is coordinated to two zinc ions in different manners, one monodentate by pyridine ring and the other by hydrazide bidentate. The angle between hydrazide and pyridine is 21.3(3)° with Zn–Zn distance of 9.1833(8) Å. The literature [11] reports that when INH is coordinated in similar way, this angle decreases with increasing Zn–Zn distance, 44.7(1)° with distance of 9.105(2) Å and 36.7(1)° with distance of 9.161(2) Å. This angle in the INH2 molecules in **1** is in agreement with this tendency, despite the different conformations observed in comparison to the structure already reported [11]. There are also some hydrogen bonds that help to stabilize its conformation, highlighted in figure S5 (N2–H2C···O23, N2–H2D···O9, and N1–H1A···O25).

Compound **1** also has a π–π stacking interaction between pyridine groups of INH1 and INH3 in the extended structure. The topological parameters [25] for this interaction are: centroide-centroid distance of 3.70(2) Å, interplanar distance of 3.37(2) Å, and horizontal displacement of 1.52(2) Å. Such interactions together with hydrogen bonds, O6–H6B···N7 and O2–H2B···N6 with, respectively, O···N distance of 2.871(9) and 2.752(8) Å, form an extended net in the diagonal of the *bc* plane (0 1 1) (figure 5). All hydrogen bonds highlighted for **1** are listed in table 2.

Knowing the differences in INH conformation in **1**, it is possible to understand how this ligand behaves in the presence of zinc ion and in specific hydrogen bonds with BDC and water. Similar to **1**, **2** shows differences in structural properties, influenced by the environment, which are detailed below.

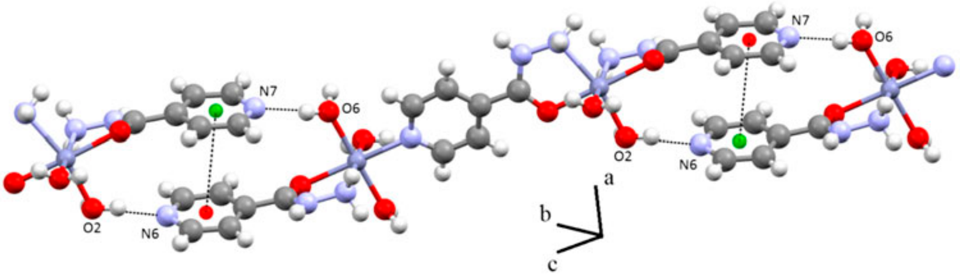


Figure 5. π–π stacking interaction in **1** between pyridine groups of INH1 and INH3 and hydrogen bonds between pyridine ring and water molecule in the extended structure.

Table 2. The most important hydrogen bonds in **1**.

Donor (D)	Acceptor (A)	Distances (Å)			Angles (°)
		D–H	H···A	D···A	D–H···A
O4–H4A	O9	0.8600	1.8700	2.707(7)	164.00
O7–H7A	O10	0.8600	1.8000	2.645(8)	165.00
O7–H7B	O14	0.8700	1.9000	2.699(7)	154.00
O3–H3B	O14	0.8600	1.9300	2.774(7)	166.00
O4–H4B	O13	0.8600	1.8500	2.664(8)	157.00
O21–H21B	O15	0.8600	1.9400	2.769(7)	161.00
O21–H21A	O11	0.8600	2.0100	2.751(9)	143.00
O22–H22B	O16	0.8500	2.0200	2.711(10)	139.00
O22–H22A	O12	0.8460	2.0240	2.8280(10)	158.44
O24–H24A	O22	0.8600	1.9600	2.816(9)	177.00
O24–H24B	O11	0.8700	1.8100	2.676(9)	175.00
N8–H8	O15	0.8600	1.9800	2.771(8)	153.00
N9–H9C	O22	0.9000	2.0100	2.908(8)	171.00
N2–H2C	O23	0.9100	2.3400	2.859(8)	116.00
N2–H2D	O9	0.9100	2.1000	2.957(7)	158.00
N1–H1A	O25	0.8600	1.9200	2.731(7)	156.00
O6–H6B	N7	0.9000	2.1500	2.871(9)	136.00
O2–H2B	N6	0.8500	1.9100	2.752(8)	170.00

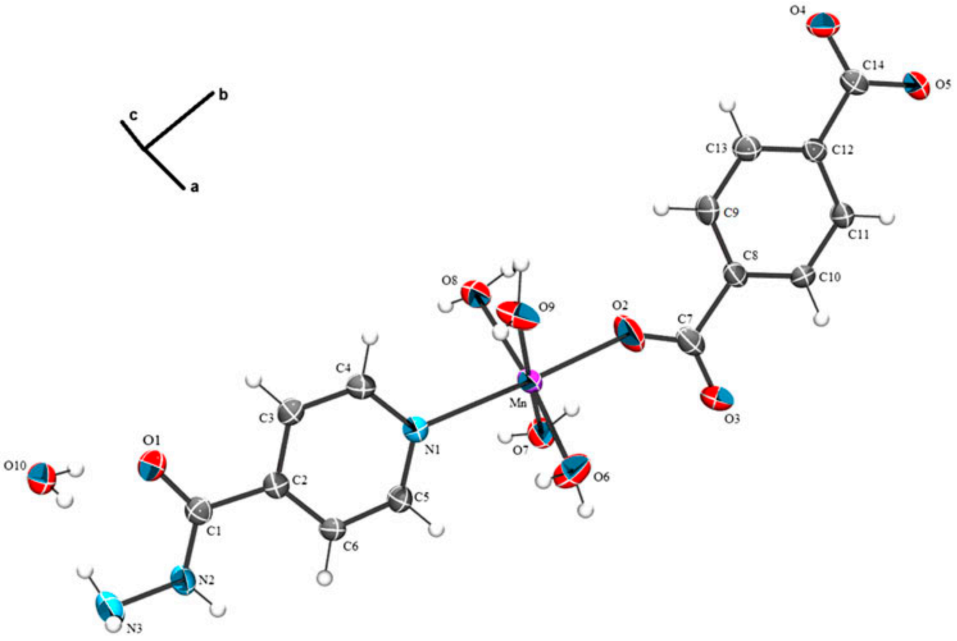


Figure 6. Crystalline structure of **2** (asymmetric unit).

The vibrational spectra for **2** are displayed in figure S6 in supplementary materials, as well as the TGA (figure S7). Table 1 shows crystallographic data for single crystal of **2**. These data show the good quality of refinement where the statistical parameters *R*, *wR*, and *S* are in agreement to the required. The refined structure of **2** is presented in figure 6.

In **2**, INH and BDC are monodentate to manganese. Its geometry is a distorted octahedron and its coordination sphere is completed by four water molecules (figure S8). The number of water molecules was confirmed by TGA (figure S7).

Analyzing the INH conformation, there are some peculiarities. The hydrazide and pyridine ring are almost coplanar, with a torsion angle of 1°, and the bond lengths are considerably different from free INH [7, 8]. These peculiarities show how coordination to manganese can change the INH conformation (table S1).

There are some important hydrogen bonds that contribute to INH conformation and in the stabilization of the structure. Figure 7 shows several of these hydrogen bonds. Some of them occur among hydrazide of INH and water (both crystallization and coordinated) and between carboxylate group of BDC and the same water molecules. These interactions are detailed in table 3 and extend the supramolecular motif along the *c* crystallographic axis, providing several interactions among the complexes in the structure that contribute stabilization. This motif is represented by $C_3^3(8)R_5^3(10)R_5^4(13)$ graph set.

Three hydrogen bonds extend the crystalline structure along the *a* crystallographic axis, O9–H9A···O4, O9–H9C···O5, and O8–H8B···O3, formed between carboxylate of BDC and coordinated water (figure 8). These hydrogen bonds extend like a chain and form a supramolecular unit of repetition in one dimensional (1-D). This motif can be represented by $C_2^2(6)R_2^2(8)$ and $C(6)$ graph set. All hydrogen bonds are listed in table 3.

Comparing **1** and **2**, it is possible to see differences in INH conformation, as well as comparing with the literature. In the reported INH coordinated to copper ion [10], the ligand does not change conformation. INH2 in **1** and INH in **2** change their conformation. These results show that the coordination can modify the INH conformation and this modification depends on the coordination mode. INH1 and INH3 in **1** are coordinated similar to

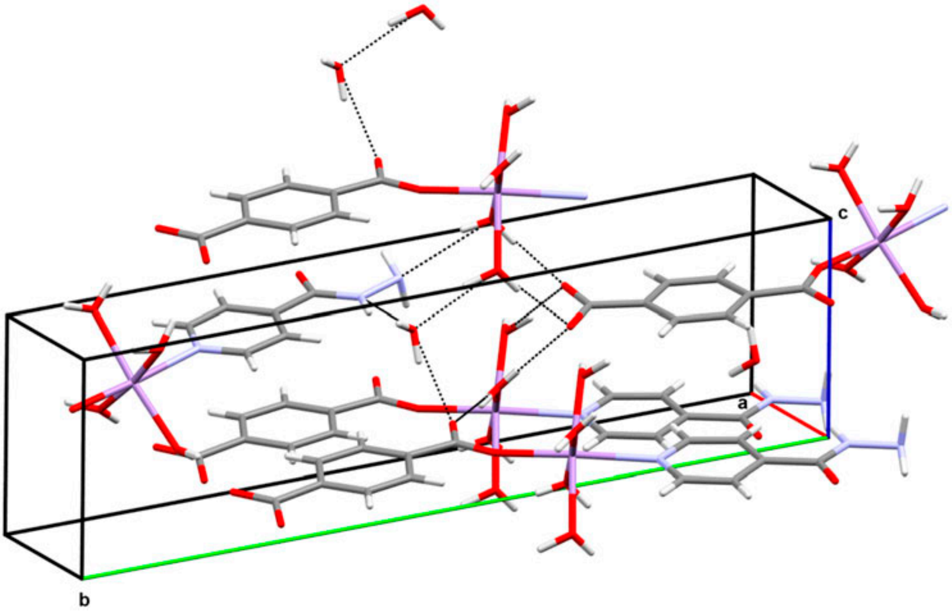


Figure 7. Hydrogen bonds in **2** between INH, BDC, and water. Some molecules were omitted for better visualization.

Table 3. The most important hydrogen bonds in **2**.

		Distances (Å)			Angles (°)
Donor (D)	Acceptor (A)	D–H	H···A	D···A	D–H···A
O6–H6A	O4	0.9400	1.7600	2.695(3)	174.00(8)
O6–H6B	N3	0.7900	2.2300	3.000(4)	166.00(4)
O7–H7A	O5	0.8400	1.9700	2.797(3)	171.00(4)
O7–H7B	O10	0.9200	1.9000	2.763(4)	157.00(5)
O8–H8A	O5	0.7300	2.0500	2.772(3)	177.00(5)
O8–H8B	O3	0.9400	1.8300	2.754(4)	168.00(5)
O9–H9A	O4	0.8700	1.8400	2.703(4)	173.00(4)
O9–H9C	O5	0.8400	1.9300	2.760(4)	168.00(4)
O10–H10A	O3	0.8400	1.9400	2.742(4)	160.00(8)
N2–H2	O10	0.8600	1.9900	2.791(4)	155.00(1)

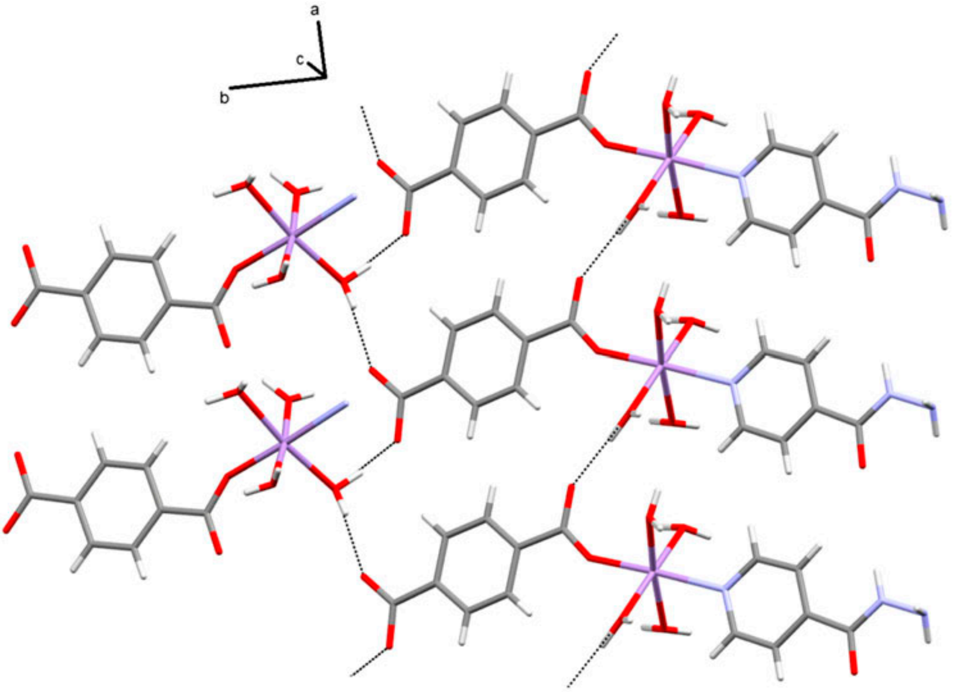
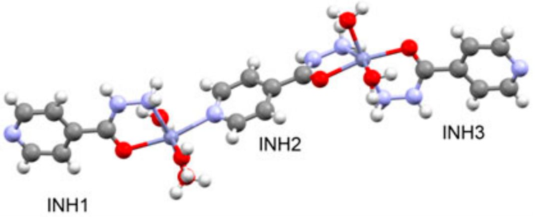


Figure 8. Hydrogen bonds in **2** along the *a* axis. Some molecules were omitted for better visualization.

compound with copper ion [10], and INH does not change in comparison to crystal structure of free INH.

There are several structures where different benzenedicarboxylic acid and nitrogen ligands are both coordinated to Zn^{2+} [26–28] or Mn^{2+} [29]. In these, there are carboxylate groups of benzenedicarboxylic acid coordinated by both oxygens (to one or two metallic centers) or just by one. Comparing it with described compounds in this work, it is notable that in **1**, BDC is not coordinated, acting only as a counter ion. In **2**, the BDC ion coordinated with one oxygen to Mn^{2+}, similar to benzenedicarboxylate reported [29].



Scheme 1. Sequence of the three distinct INH present in **1** and with different Zn metallic centers.

4. Conclusion

The two synthesized compounds were characterized by elemental analysis, FT-IR, Raman, TGA, and X-ray diffraction by single crystal that allows a complete supramolecular analysis.

The crystal analyzed for **1** is twinned, but its crystallographic data could be treated for non-merohedral twinning. Its refined structure shows three distinct INH molecules and five water molecules coordinated to two Zn^{2+}, neutralized by two BDC ions and also five crystallization water molecules. INH1 and INH3 have the same conformation, coordination modes and participate in similar hydrogen bonds. These INH molecules also have a π–π stacking interaction and extended the structure in the diagonal of the *bc* plane. INH2 shows a different conformation which can be associated to coordination mode and Zn–Zn distance.

Compound **2** is simpler than **1**, formed by one INH, one BDC, four coordinated, and one crystallization water. The INH is almost coplanar and there are some important hydrogen bonds in the structure. The coordination of INH to Mn^{2+} promotes changes in some bond lengths like C–C and C–N in INH molecules in the solid state.

In these two compounds, the presence of BDC and water is very important in stabilization of the complex and in INH conformation. The BDC ion in **1** is different from some structures already reported [26–29] and that in **2**, BDC coordinated as expected by one oxygen of carboxylate.

Supplementary material

CCDC 986721 and 986722 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center at www.ccdc.cam.ac.uk/data_request/cif. Other support information can be obtained in the article journal site.

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References

[1] J.W. Steed, J.L. Atwood. *Supramolecular Chemistry*, 2nd Edn, Wiley, Chichester (2009).
[2] I. Sarcevica, L. Orola, M.V. Veidis, A. Podjava, S. Belyakov. *Cryst. Growth Des.*, **13**, 1082 (2013).
[3] P. Grobelny, A. Mukherjee, G.R. Desiraju. *CrystEngComm*, **13**, 4358 (2011).
[4] A. Lemmerer, J. Bernstein, V. Kahlenberg. *CrystEngComm*, **12**, 2856 (2010).
[5] A. Lemmerer, J. Bernstein, V. Kahlenberg. *J. Chem. Crystallogr.*, **41**, 991 (2011).
[6] M.V.N. de Souza, H.R.A. Vasconcelos. *Quím. Nova*, **28**, 678 (2005).
[7] L.H. Jensen. *J. Am. Chem. Soc.*, **76**, 4663 (1954).
[8] T.N. Bhat, T.P. Singh, M. Vijayan. *Acta Crystallogr., Sect. B: Struct. Sci.*, **30**, 2921 (1974).
[9] J.C. Hanson, N. Camerman, A. Camerman. *J. Med. Chem.*, **24**, 1369 (1981).
[10] Z.J. Jiang, P.S. Zhao, R.Q. Li, L.T. An, Z.C. Zhang, J. Xu. *J. Chem. Crystallogr.*, **43**, 463 (2013).
[11] M.C.R. Freitas, J.M.S. António, R.L. Ziolli, M.I. Yoshida, N.A. Rey, R. Diniz. *Polyhedron*, **30**, 1922 (2011).
[12] F.B. de Almeida, F.H. e Silva, M.I. Yoshida, H.A. de Abreu, R. Diniz. *Inorg. Chim. Acta*, **402**, 60 (2013).
[13] J. Kim, U. Lee, B.K. Koo. *Bull. Korean Chem. Soc.*, **31**, 1743 (2010).
[14] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim. *Nature*, **423**, 705 (2003).
[15] H. Chun, D.N. Dybtsev, H. Kim, K. Kim. *Chem. Eur. J.*, **11**, 3521 (2005).
[16] *CrysAlis RED*, 1.171.35.15; Oxford Diffraction Ltd, Oxford (2008).
[17] G.M. Sheldrick. *Acta Crystallogr., Sect. A*, **64**, 112 (2008).
[18] C.L. Barnes. *J. Appl. Crystallogr.*, **30**, 568 (1997).
[19] C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van de Streek. *J. Appl. Crystallogr.*, **39**, 453 (2006).
[20] S. Anger, D. Bayer, C. Dailey, A. Dilger, S. Demlow, A. Enzmann, D. Farmer, J. McElhiney, R. Parker, E. Schwan, R. Wegner, C. Young. *Persistence of Vision Raytracer (Version 3.6)*, Persistence of Vision Pty. Ltd, Victoria (2004). Retrieved from http://www.povray.org/download/.
[21] K. Momma, F. Izumi. *J. Appl. Crystallogr.*, **44**, 1272 (2011).
[22] P. Müller, R. Herbst-Irmer, A.L. Spek, T.R. Schneider, M.R. Sawaya. *Crystal Structure Refinement*, Oxford University Press, New York (2006).
[23] G.B. Jameson. *Acta Crystallogr., Sect. A*, **38**, 817 (1982).
[24] M.C. Etter, J.C. MacDonald, J. Bernstein. *Acta Crystallogr., Sect. B: Struct. Sci.*, **46**, 256 (1990).
[25] D. Braga, L. Maini, F. Grepioni. *Chem. Eur. J.*, **8**, 1804 (2002).
[26] B. Wang, Y.-B. Xie, H. Yang, M. Li, J.-R. Li. *J. Coord. Chem.*, **67**, 3484 (2014).
[27] S.M. Keltie, P.A. Gale, M.E. Light, M. Tromp. *J. Coord. Chem.*, **66**, 3058 (2013).
[28] P.-F. Yao, C.-J. Ye, F.-P. Huang, H.-D. Bian, Q. Yu, K. Hu. *J. Coord. Chem.*, **66**, 1591 (2013).
[29] X. Zhu, S. Zhao, Y.-F. Peng, B.-L. Li, H.-Y. Li. *J. Coord. Chem.*, **67**, 1317 (2014).