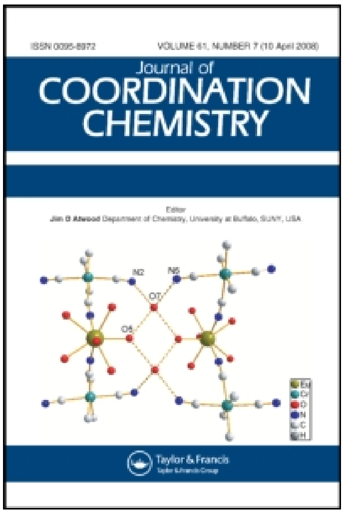

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Synthesis, characterization, and crystal structure of the 3-D metal organic framework $\{[Ba(in)(H_2O)_6][in]\}_\infty$

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We present a barium metal–organic framework $\{[Ba(in)(H_2O)_6][in]\}_\infty$ prepared *via* a simple acid–base reaction between $BaCO_3$ and inH (inH = 4-pyridinecarboxylic acid). The complex crystallizes in the monoclinic space group $P2_1/c$ ($a = 6.2592(18)$, $b = 44.289(12)$, $c = 7.2754(15)$; $\alpha = \gamma = 90$, $\beta = 118.890(18)$; $V = 1765.8(8)$ Å^3) displaying an unusual ion association mode with half of the anions metal-bound, whereas the others are associated *via* a hydrogen-bonded and $\pi \cdots \pi$ stacking network. Among the coordinated anions, the carboxylate functionalities bridge the metal centers.

Keywords: Barium; Alkaline earth; Heavy metal; Metal organic frameworks; Nitrogen-based ligands

1. Introduction

A topic of interest in metal–organic framework (MOF) chemistry includes the use of rigid linkers which contain mixed donors. This type of organic linker greatly influences the properties of the frameworks affecting stability and accessibility of the metal centers [1]. Previous reports have shown that the use of linkers containing mixed donors afford a range of coordination environments that mainly depends on the nature of the metal centers. Figure 1 illustrates the different metal–ligand binding modes reported for aryl carboxylate ligands [1, 2]. The inH (inH = 4-pyridinecarboxylic acid) used in this work adds complexity through the pyridyl function, which may be involved in the creation of a network. Carboxylate–pyridine combinations in a ligand system afforded previous 3-D transition metal MOFs, including a porous MOF based on Mn [3]. Other examples include the isostructural complexes $[Zn(in)_2(H_2O)_4]$ and $[Cd(in)_2(H_2O)_4]$ [4], where the ligand coordinates through its carboxylate and nitrogen donors. Remarkably, the increase in metal size from Zn to Cd did not affect the overall structural features.

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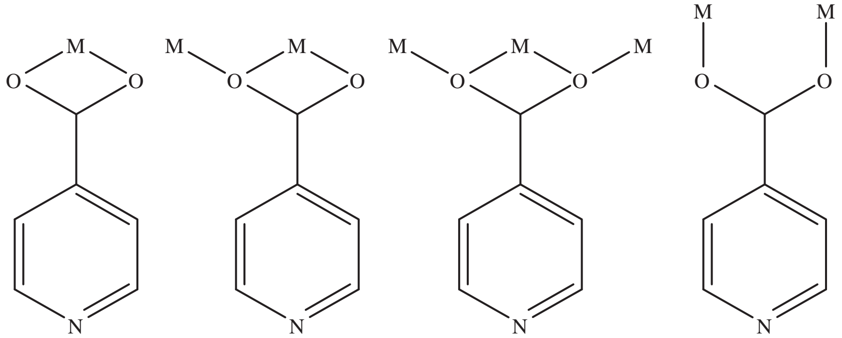

Figure 1. Different binding modes for isonicotinate. Metal pyridine nitrogen coordination is not shown.

In contrast to the extensive work on transition metal MOFs, little is known on the s-, p-, and f-block analogs. An example of a porous–alkali-based MOF exhibiting gas sorption properties includes $[Li(in)] \cdot 0.5$ DMF, available by a solvothermal reaction between LiOH and inH in dimethyl formamide (DMF) [5]. The channels in this compound are occupied by DMF molecules. Alkaline earth metal analogs based on the isonicotinic acid ligand system include $\{[Mg(in)_2(H_2O)_4]\}$ [6], where the ligand coordinates through its pyridyl nitrogen and one of the carboxylate oxygens. Further association is provided by an extensive network of hydrogen bonding through the four waters coordinated to the metal. The magnesium center is six coordinate and can be regarded as a distorted octahedron. Recently, calcium $\{[Ca(in)_2(H_2O)_4]\}$ and strontium $\{[Sr(in)(H_2O)_6][in]\}$ MOFs based on isonicotinic acid have also been reported [7]. In contrast to the magnesium species, and expressing the increase in metal size, both carboxylate oxygens and the ligand's *para* nitrogen participate in coordination to Ca(II). In this example the calcium center is seven coordinate with a capped octahedral geometry. Similar to the magnesium analog, the 3-D network structure is afforded by extensive hydrogen bonding through its four water molecules in addition to $\pi \cdots \pi$ stacking contacts.

In line with the trend observed upon descending group II, the strontium complex displays an eight coordinate metal center, where two of the coordination sites are occupied by carboxylate moieties, in addition to six waters. The carboxylates bind μ_2-$\eta^1:\eta^1$. The overall metal environment can be described as dodecahedral. One ligand binds to the metal center while the other is not metal bound. The $[Sr(in)(H_2O)_6]_\infty$ layers associate *via* hydrogen-bonding and $\pi \cdots \pi$ stacking (3.502(3)–3.611(3) Å) interactions with the unassociated ligands affording a 3-D framework. This arrangement of coordinated and unassociated ligands is not observed for the magnesium and calcium species. A related eight-coordinate barium environment is observed in the anhydrous, heteroleptic poly[μ_4-isonicotinato-μ_3-nitrato-barium(II)] ($[Ba(in)(NO_3)]_n$) [8]. In analogy to the strontium compound, $[in]^-$ bridges the metal centers, the presence of the non-coordinated NO_3^- anion results in significantly different structural features.

Here, we report on our work to further illuminate the influence of metal radius on the overall structural features of isonicotinate-based MOF's by preparation and characterization of a barium isonicotinate complex.

2. Experimental

2.1. *Physical measurements*

All chemicals were obtained commercially and used without purification (purity of $BaCO_3$ – 98%, 4-pyridinecarboxylic acid – 99%). Reactions were carried out in distilled water. IR measurements were carried out as mineral oil mulls in KBr discs in a Nicolete IR200 FT-IR spectrophotometer from 4000 to 500 cm^{-1}. Thermogravimetric analysis (TGA) measurements were performed on a TGA Q500 series instrument (TA Instruments-Waters LLC) under an N_2 balance/sample purge flow of 40 and 60 mL min^{-1}, respectively. The sample (wt 7.9640 mg) was loaded onto a platinum pan and heated using a ramp method from room temperature to 750°C. All crystal data were collected using a Bruker SMART system with a three-circle goniometer and an APEX-CCD detector. Data were collected using Mo-Kα radiation at 103(2) K using a low-temperature device built by H. Hope (UC Davis).

The crystals were submerged in highly viscous hydrocarbon oil (Infineum), mounted on a glass fiber and placed in the low-temperature stream on the diffractometer, as described in detail previously [9]. Data collection parameters and refinement details have been described [9]. The crystal structure was solved using direct methods and subsequent refinement by full-matrix least-squares on F^2 [10]. All non-hydrogen atoms were refined anisotropically. Hydrogens, except those of water, were calculated to fixed positions using restraints. Hydrogens in water were located directly in the difference map. An absorption correction was performed using SADABS [11]. Centroid to centroid distances representing $\pi \cdots \pi$ contacts were calculated using the OLEX2 crystallographic suite [12]. Further details about the refinements are outlined in the "Supplementary material". Powder diffraction experiments were conducted on a Bruker D8 Advance Series II, equipped with a copper source and a NaI scintillation counter. The powder diffraction data were recorded at room temperature on a sample that was kept at 130°C for 1.5 h to induce dehydration.

2.2. *Synthesis and characterization*

$\{[Ba(in)(H_2O)_6][in]\}_\infty$: A slight excess of $BaCO_3$ (493.3 mg, 2.5 mmol) and inH (492.8 mg, 4 mmol) were combined in 25 mL of distilled water. The resulting slurry ($BaCO_3$ is insoluble under these conditions) was stirred and kept under reflux for 24 h, after which the colorless suspension was filtered hot using a Whatman No. 3 filter. The resulting clear, colorless mother liquor was allowed to cool to room temperature and within a few days, colorless block-shaped crystals suitable for X-ray crystallography were collected. Gentle heating (130°C) for 1.5 h, afforded the dehydrated target compound, the transparent crystals turned opaque in the process. Powder diffraction experiments were conducted to verify if the crystal lattice would remain intact after the desolvation process. M_p = above 400°C. Yield (non-optimized): 23.38%. IR(cm^{-1}): 3415.43 (s), 2351.74 (w), 1600.23 (w), 1549.45 (w), 1057.93 (w).

2.3. *Structural analysis*

Crystallographic analysis revealed that $\{[Ba(in)(H_2O)_6][in]\}_\infty$ crystallizes in the monoclinic $P2_1/c$ space group (table 1) and is isostructural to the previously reported

Table 1. Crystallographic data and structural refinement for $\{[Ba(in)(H_2O)_6][in]\}_\infty$.

Empirical formula	$C_{12}H_{20}BaN_2O_{10}$
Formula weight	489.64
Crystal system	Monoclinic
Space group	$P2_1/c$
Temperature (K)	103(2)
Unit cell dimensions (Å, °)	
a	6.2592(18)
b	44.289(12)
c	7.2754(15)
α, γ	90
β	118.890(18)
Volume (Å^3), Z	1765.8(8), 4
Calculated density (Mg m^{-3})	1.842(8)
Absorption coefficient (mm^{-1})	2.303
2θ range for data collection (°)	0.92–28.33
Unique reflections	4373
Total reflections	17527
Goodness-of-fit on F^2	1.358
R indices (all data)	$R_1 = 0.0473$, $wR_2 = 0.0780$
Final R indices	$R_1 = 0.0435$, $wR_2 = 0.0763$
$F(000)$	968

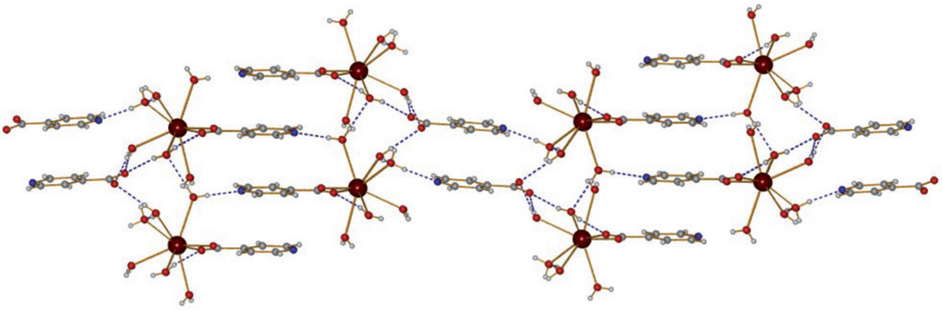

Figure 2. 2-D layers associated *via* $\pi\cdots\pi$ interactions and hydrogen bonding to form a 3-D framework.

strontium compound [7]. The target complex displays a 3-D framework *via* hydrogen-bonding network between metal coordinated water and $\pi\cdots\pi$ interactions between parallel aromatic rings. The structure contains an unassociated isonicotinate that is instrumental in forming the 3-D network through non-covalent interactions. Of particular importance to the formation of the 3-D network is $\pi\cdots\pi$ stacking between the non-metal bound ligands with contacts between 3.532(3) and 3.648(3) Å, as shown in figure 2. The metal centers are eight coordinate, with six of the coordination sites belonging to waters; Ba–water distances range from 2.766(3) to 2.838(3) Å (table 2). These distances agree with literature values [13, 14]. The eight-coordinate metal center adopts a distorted dodecahedral geometry, with two coordination sites occupied by two carboxylate oxygens from two different isonicotinate ligands that bridge the metal centers in a μ_2-$\eta^1:\eta^1$-coordination mode and Ba–O distances of

Table 2. Selected bond lengths (Å) and angles (°) for $\{[Ba(in)(H_2O)_6][in]\}_\infty$.

Ba(1)–O(16)	2.684(3)	O(15)w–Ba(1)–O(16)	102.69(9)
Ba(1)–O(15)	2.689(3)	O(25)w–Ba(1)–O(1)w	68.98(10)
Ba(1)–O(12)w	2.766(3)	O(15)–Ba(1)–O(19)w	70.12(11)
Ba(1)–O(11)w	2.791(3)	O(16)–Ba(1)–O(19)w	85.08(11)
Ba(1)–O(19)w	2.811(3)	O(11)w–Ba(1)–O(1)w	116.13(10)
Ba(1)–O(1)w	2.813(3)	O(16)–Ba(1)–O(10)w	140.03(10)
Ba(1)–O(10)w	2.838(3)	O(15)–Ba(1)–O(10)w	71.55(10)

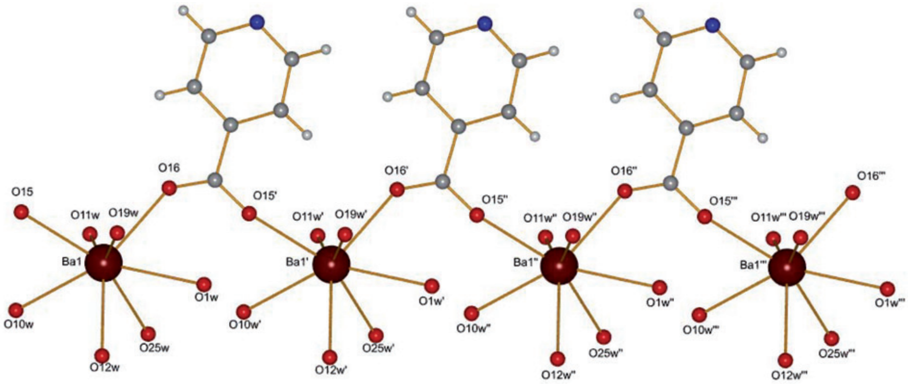

Figure 3. Zig-zag 1-D chains. Hydrogens in water and hydrogen bonding are removed for clarity.

2.684(3) and 2.689(3) Å, resulting in a 1-D zig-zag-like chain as shown in figure 3. The zig-zag chains are connected by hydrogen bonds (table 3, figure 4) and $\pi \cdots \pi$ interactions from the metal bound ligands (3.642(2) Å) into 2-D layers, as shown in figure 2. All $\pi \cdots \pi$ stacking values are in agreement with literature values [15]. Despite the significant increase in ionic radius from strontium to barium (1.27–1.43 Å, Δ0.16 Å) [16], the overall structural features for the strontium and barium complexes are quite similar, with the increase in expected bond length due to the increased metal radius. The larger metal radius also results in an increase in structural flexibility, as expressed by the slightly larger range of O–Ba–O angles (66.61(9)–150.07(10)°), as compared to the strontium congener (67.0(1)–148.0(1)°).

2.4. *Thermogravimetric analysis*

TGA (figure 5) shows a decrease of 21.61 wt% until 124°C, corresponding to the loss of six coordinated waters (Calcd 22.06%). The compound appears to be stable until 490°C, where a further 22.41 wt% drop is observed, indicating decomposition of the compound.

2.5. *Powder diffraction studies*

The importance of coordinated water on the integrity of the structure was demonstrated by powder diffraction studies of the dehydrated complex, obtained by heating the bulk

Table 3. Selected hydrogen bonding distances (Å) for $\{[Ba(in)(H_2O)_6][in]\}_\infty$.

D–H···A	d(D···A)
O(25)–H(62)···N(3)	2.769
O(11)–H(70)···N(2)	2.756
O(10)–H(64)···O(25)	2.825
O(1)–H(61)···O(8)	2.770
O(25)–H(63)···O(8)	2.852

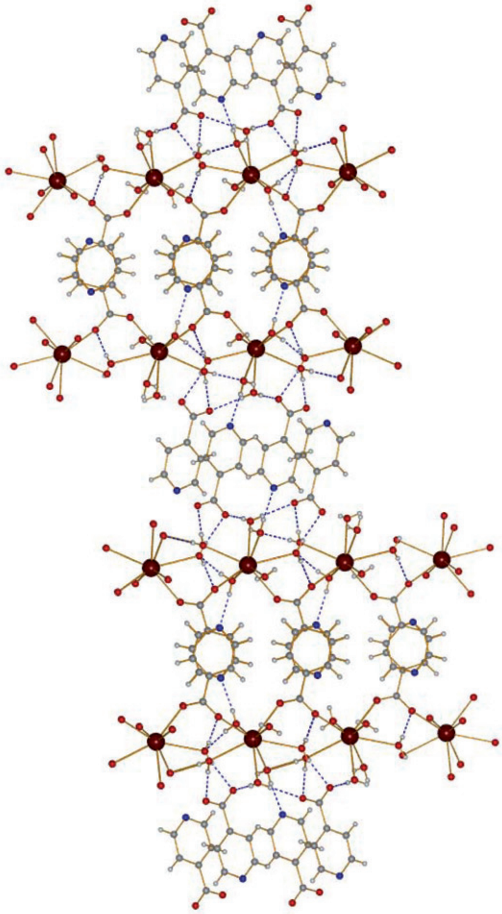

Figure 4. 3-D network showing hydrogen bonds (dashed lines) based on 1-D chains connected into 2-D sheets by non-covalent interactions.

sample at 130°C for 1.5 h. The temperature of 130°C was chosen according to TGA data that suggest complete dehydration at 124°C and thermal stability of the resulting species until 490°C.

Comparison of the calculated powder pattern of the hydrated compound from single crystal data with those of the dehydrated compound show the loss of crystallinity,

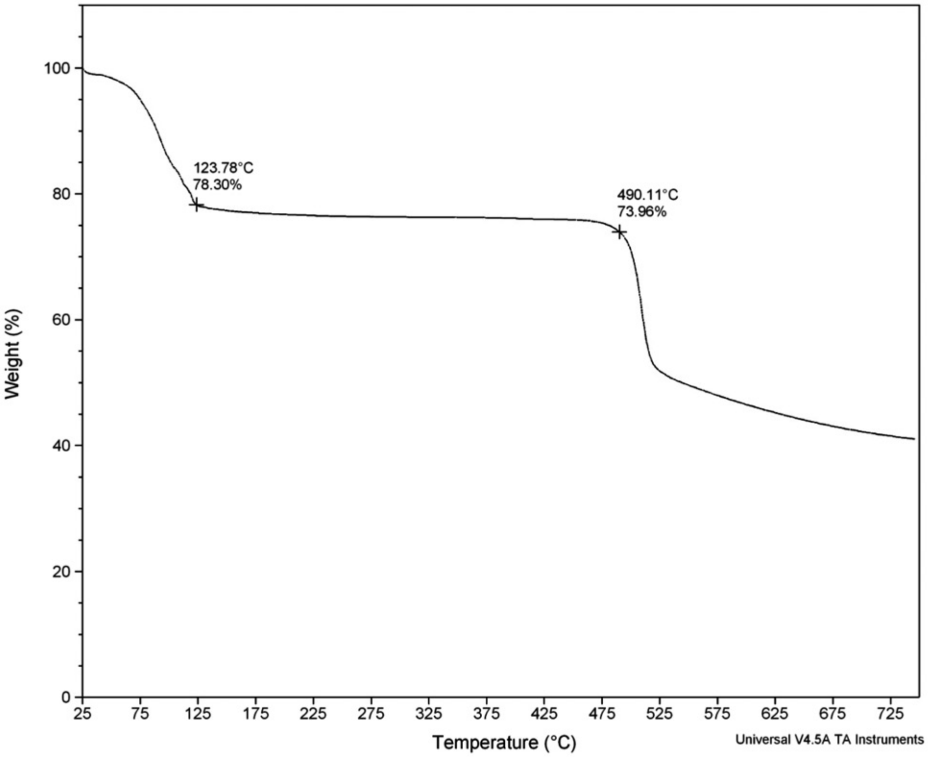

Figure 5. TGA plot for $\{[Ba(in)(H_2O)_6][in]\}_\infty$ that shows stepwise loss of water molecules (~124°C), thermal stability, and consequent decomposition (490°C).

leading to the conclusion that the crystalline lattice disintegrates upon the loss of water. This conclusion is in agreement with the inspection of the sample, which turns from transparent to opaque upon heating.

3. Conclusions

In summary, a barium MOF $\{[Ba(in)(H_2O)_6][in]\}_\infty$ which exhibits an unusual ion association mode with one metal-coordinated and one unassociated ligand has been synthesized *via* simple acid–base chemistry. Unexpectedly, the compound is isostructural to the strontium congener. The barium centers coordinate in a μ_2-$\eta^1:\eta^1$-bridging motif to the ligand's carboxylate oxygens resulting in zigzag 1-D chains. These chains are associated into 2-D layers *via* hydrogen-bonding and $\pi\cdots\pi$ interactions. The non-metal bound counteranion enables linkage of the layers *via* an extensive network of hydrogen bonding and $\pi\cdots\pi$ interactions affording a 3-D framework. This work clearly demonstrates that a change in metal size does not necessarily result in a change in structural features. This observation strongly suggests the continued need for individual analysis of solids, as the prediction of the respective solid-state structures is not yet possible.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication, No. CCDC 794948. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge C21EZ, UK (Fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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