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Functionalized aminocarboxylate moieties as linkers for coordination polymers: Influence of the substituents in the dimensionality of the final structure.

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The evaluation of aminocarboxilic acid derivatives as linker precursors for amine or hydroxyl tagged extended structures is described. The effect of the presence of an additional functionality in the ring is also explored. In order to analyze the influence of position or nature of this functional group, we studied the related aminocarboxilic acids: 3,4-diaminocarboxilic acid (3,4-dabaH), 3,5-diaminocarboxilic acid (3,5-dabaH), 4-amino-3-hydroxycarboxilic acid (4,3-ahbaH) and 3–amino-4-hydroxycarboxilic acid (3,4-ahbaH). Although these are very simple, commercial ligand precursors, there are very few examples reported with them coordinated. In fact, no compounds have been described with 4,3-ahba or 3,4-ahba as ligands. This work has allowed us to isolate four new compounds of diverse dimensionality, $[Zn(3,4\text{-}daba)_2(H_2O)]_n$ (**1**), $\{[Zn(3,5\text{-}daba)(py)(OH_2)](NO_3)\}_n$ (**2**), $[Zn(4,3\text{-}ahba)_2(Py)_2]$ (**3**) and $[Zn(bipy)_2(4,3\text{-}ahba)_2]_2$ (**4**) (py = pyridine, bipy = 4,4'-bipyridine). Derivatives **1** and **2** present extended structures with uncoordinated amine groups. However in our attempt to obtain hydroxyl tagged species, we observed that the presence of the OH group hampers the possibility of generating extended structures due to the formation of strong intermolecular interaction motifs.

Introduction

Although coordination polymers (CPs) have been known for many years, the interest in this kind of compounds has exponentially increased since the beginning of the century.[1] Particularly those that are porous, such as metal-organic frameworks (MOFs), awake huge interest not only because of their attractive structures, but also due to their potential to be used as functional materials.[2,3] As such, MOFs have found application in areas as diverse as medicinal chemistry,[4] gas storage,[5] luminiscence,[6] catalysis[7] and molecular sensing.[8]

An important advantage of CPs when compared to inorganic solids, relies on the fact that the introduction of different functional groups into CPs is more straightforward as these frameworks possess an organic component suitable for installing any number of chemical moieties. As such, the possibility of introducing different functionalities into the network together with the intrinsic high ordered structure implies that these functional groups will be homogenously distributed within the framework and it will be possible to control the distance between them by choosing the right organic connectors.

Clearly a way of enlarging the applications for these species would be to incorporate complex functional groups in the network. However, the main limitation in the functionalities that can be present in the organic linkers used is the way in which many of these derivatives are synthetized. As such, in many cases they are prepared using solvothermal methods that imply high temperature and pressure. In these conditions there are functional groups that degrade and do not survive the synthesis process. That is why the idea of performing a functionalization as a step post-synthesis was proposed,[9] being specially from 2007 onwards when the huge potential of this synthetic strategy has been clearly evidenced.[10] Using this methodology, the chemical modification can be done on the material once it has been synthesized and limitations due to the synthetic method used for obtaining the material are avoided.

In our group we are focused in the preparation of derivatives with amine or hydroxide uncoordinated groups. Both functional groups are appropriate moieties to be modified by applying well known organic chemical transformations. The amine functionality can also be a donor group able to coordinate metallic fragments, rendering the coordination framework into a polymeric ligand. This possibility opens the option of using the CPs as potential metallodrug carriers. As such a very popular family of anticancer metallodrug is the arene-Ru(II) derivatives,[11] these compounds could coordinate to an amino moiety dangling from the MOF since it is well known the affinity of Ru(II) to coordinate nitrogen donor groups.[12]

In this context, aminobenzoic acids are attractive linker precursors since they are molecules of biological importance and also could coordinate either by the carboxylate or the amine groups or both.[13] The preparation of zinc derivatives with these ligands is of particular interest, since zinc is active in many biological processes. Besides, zinc complexes with ligands derived from molecules of natural origin, such as aminoacids or vitamins, have proven to be active drugs in diabetes or lung diseases.[14]

Another interesting point of zinc complexes with aminobenzoates is that due to the low toxicity of the species formed they could be good candidates as drug carriers. However a CSD search evidence that very few zinc aminobenzoate CPs have been described.[15] As such, only eleven derivatives have been reported containing either 4-aminobenzoate or 2-aminobenzoate linkers.[16,17]

Aiming to obtain aminobenzoate zinc extended structures with uncoordinated functional groups, we have extended our studies to acids related to 4-abaH that show an additional functional group in *meta* or *para* position. Our interests is directed in two ways, to know the effect on the final structure of an additional functionality in the ring and to generated derivatives with amine or hydroxide uncoordinated groups. As such, we have studied the aminobenzoic acids: 3,4-diaminobenzoic acid (3,4-dabaH), 3,5-diaminobenzoic acid (3,5-dabaH), 4-amino-3-hydroxybenzoic acid (4,3-ahbaH) and 3-amino-4-hydroxybenzoic acid (3,4-ahbaH) (figure 1). Although these are very simple, commercial ligand precursors, surprisingly enough there are very few examples with them coordinated.[15] No compounds have been described with 4,3-ahba or 3,4-ahba as ligands and for 3,4-daba only five examples have been reported with Na, Sn, Ga or Nd as metals,[18,19] none with zinc. As a comparison we have also included in this study the 4-aminobenzoic acid (4-abaH).

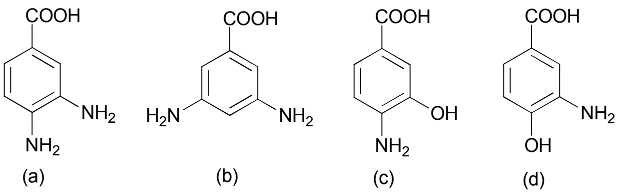


Figure 1. a) 3,4-dabaH. b) 3,5-dabaH. c) 4,3-ahbaH, d) 3,4-ahbaH

In this contribution we present our results on the evaluation of several aminobenzoic acids as linker precursors for extended structures and the analysis of the influence of an additional functional group in the aromatic ring. This work has allowed us to isolate four new compounds of diverse dimensionality, $[Zn(3,4\text{-daba})_2(H_2O)]_n$ (**1**), $\{[Zn(3,5\text{-daba})(py)(H_2O)](NO_3)\}_n$ (**2**), $[Zn(4,3\text{-ahba})_2(Py)_2]$ (**3**) and $[Zn(bipy)_2(4,3\text{-ahba})_2]_2$ (**4**), together with $\{[Zn(bipy)(p\text{-aba})_2]\cdot(bipy)(H_2O)\}_n$ (**5**) where the CP present, $[Zn(bipy)(p\text{-aba})_2]_n$, had been previously reported. Derivatives **1** and **2** show extended structures with uncoordinated amine groups. However in our attempt to obtain hydroxyl tagged species, we observed that the presence of the OH group hampers the possibility of generation of extended structures due to the formation of strong intermolecular interaction motifs.

Experimental details

General Considerations. All reagents and solvents were commercially obtained (Aldrich) and used without further purification. Distilled water was used for synthetic manipulations. NMR spectra were recorded at 400.13 (^{1}H), and 100.60 (^{13}C) MHz on a Bruker AV400. Chemical shifts (δ) are given in ppm using D_2O as solvent. ^{1}H resonances were measured relative to solvent peaks considering TMS δ = 0 ppm. Elemental analyses were obtained on a Perkin-Elmer Series II 2400 CHNS/O analyzer.

Synthesis of $[Zn(3,4\text{-daba})_2(H_2O)]_n$ (1). A mixture of 100 mL 0.11 g of $Zn(AcO)_2\cdot 2H_2O$ (0.5 mmol), 0.07 g, of 3,4-diaminobenzoic acid (0.5 mmol) and 50 mL of H_2O is heated at 100ºC for 48 h. Then the mixture is cooled down to room temperature and filtered. Brown crystals were isolated after slow evaporation. Yield: 0.06 g (27 %). Anal. Calcd for $C_{14}H_{22}N_4O_8Zn$: C, 38.24; H, 5.04; N, 12.74. Found C, 37.81; H, 4.87; N, 12.54.

Synthesis of $\{[Zn(3,5\text{-daba})(py)(H_2O)](NO_3)\}_n$ (2). A mixture of 0.24 g (0.8 mmol) of $Zn(NO_3)_2\cdot 6H_2O$, 0.24 g (1.6 mmol) of 3,5-diaminebenzoic acid, 0.6 mL (7.4 mmol) of pyridine, 0.8 mL of H_2O and 2 mL of 1-propanol was sealed in a 50mL Teflon-lined autoclave and heated at 75ºC for 32 hours. Then the autoclave was slowly cooled to room temperature. The mixture was filtered and compound **2** was isolated as black crystals. Also the compound could be isolated from the mother liquor by slow evaporation. Yield: 0.17 g, 58%. Anal. Calcd for $C_{12}H_{14}N_4O_6Zn$: C, 38.4; H, 3.8; N, 14.9. Found: C, 37.7; H, 3.5; N, 14.5.

Synthesis of $[Zn(4,3\text{-ahba})_2(py)_2]$ (3). A mixture of 0.24 g (0.8 mmol) of $Zn(NO_3)_2\cdot 6H_2O$, 0.24 g (1.6 mmol) of 4-amino-3-hidroxibenzoic acid, 0.6 mL (7.4 mmol) of pyridine, 0.8 mL of H_2O and 2 mL of 1-propanol was sealed in a 50mL Teflon-lined autoclave and heated at 75ºC for 32 hours. Then the autoclave was slowly cooled to room temperature. The mixture was filtered and compound **3** was isolated as brown crystals. Yield: 0.18 g 43%. ^{1}H RMN (D_2O, 400MHz, 293K, δ ppm): 8.54 (d, $^3J_{HH}$ = 5 Hz, 2H, py), 7.91 (t, $^3J_{HH}$ = 8 Hz, 1H, py), 7.49 (t, $^3J_{HH}$ = 7 Hz, 2H, py), 7.37 (s, 1H, 4,3-ahba), 7.36 (s, 1H, 4,3-ahba), 6.87 (d, $^3J_{HH}$ = 9 Hz, 1H, 4,3-ahba). Anal. Calcd for $C_{24}H_{22}N_4O_6Zn$: C, 54.61; H, 4.20; N, 10.61. Found: C, 54.43; H, 4.31; N, 10.56

Synthesis of $[Zn(bipy)_2(4,3\text{-ahba})_2]_2$ (4) 0.24 g (0.8 mmol) of $Zn(NO_3)_2\cdot 6H_2O$, 0.24 g (1.6 mmol) of 4-amino-3-hydroxibenzoic acid and 1.16 g (7.4 mmol) of bipyridine were dissolved in a mixture of 0.8 mL of H_2O and 2 mL of 1-propanol and placed in a 50mL Teflon-lined autoclave. The reaction mixture was heated at 75ºC for 32 hours. After slow cooling the solution is filtered. Compound **4** is isolated as orange crystals. Yield: 0.29 g, 54%. Anal. Calcd for $C_{68}H_{58}N_{12}O_9Zn_2\cdot H_2O$: C, 61.12; H, 4.53; N, 12.58. Found: C, 60.85; H, 4.23; N, 12.4.

Synthesis of $\{[Zn(bipy)(p\text{-aba})_2]\cdot(H_2O)(4,4'\text{-bipy})]\}_n$ (5) A mixture of 0.17 g (0.8 mmol) of $Zn(AcO)_2\cdot 2H_2O$, 0.22 g (1.6 mmol) of *p*-aminobenzoic acid, 1.16 g (7.4 mmol) of bipyridine, 0.8 mL of H_2O and 2 mL of 1-propanol was sealed in a 50 mL Teflon-lined autoclave and heated at 75ºC for 32 hours. Then the autoclave was slowly cooled to room temperature. The mixture was filtered and compound **5** is isolated as brown crystals. Yield:

0.16 g, 32%. Anal. Calcd for $C_{68}H_{58}N_{12}O_9Zn_2$: C, 61.96; H, 4.43; N, 12.75. Found: C, 61.7; H, 4.8; N, 12.3

Single-Crystal X-ray Structure Determination of 1-5.

Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in Table 1. Suitable single crystals of compounds **1** to **5** for the X-ray diffraction study were selected. Data collection was performed on a crystal stuck to a glass fiber using an inert perfluorinated ether oil and mounted in a low temperature N_2 stream 200(2) K, in a Bruker-Nonius Kappa CCD single crystal diffractometer equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), and an Oxford Cryostream 700 unit. Details of data collections are summarized in table 2. Raw data were corrected for Lorenz and polarization effects. The structures were solved, using the WINGX package,[20] by direct methods (SHELXS-97) , completed by the subsequent difference Fourier Techniques and refined by using full-matrix least-squares against F^2 (SHELXL-97).[21] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 992467-962471 Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)

Table 1. Crystallographic data

Compound	1	2	3	4	5
Formula	$C_{14}H_{22}N_4O_8Zn$	$C_{12}H_{14}N_4O_6Zn$	$C_{24}H_{22}N_4O_6Zn$	$C_{68}H_{56}N_{12}O_{12}Zn_2$	$C_{68}H_{58}N_{12}O_9Zn_2$
FW	439.73	375.64	527.83	1363.99	1318.00
Cryst syst	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$Pccn$	$P2_1/n$	$Pbcn$	$P2_1/n$	$P\text{-}1$
a (Ǻ)	8.0133(7)	8.764(2)	7.933(2)	9.9100(9)	9.404(2)
b (Ǻ)	11.2963(4)	15.381(4)	13.2295(17)	16.496(3)	11.9230(17)
c (Ǻ)	19.9503(13)	11.395(2)	22.388(5)	18.716(3)	14.556(3)
α(°)					77.240(10)
β (°)	90	106.617(10)	90	104.910(8)	84.170(10)
γ(°)					72.490(10)
V (Ä^3)	1805.9(2)	1471.8(6)	2349.5(9)	2956.6(8)	1516.9(5)
F(000)	912	768	1088	1408	682
μ/mm^{-1}	1.412	1.707	1.094	0.890	0.861
Z, ρ_c (g.cm^{-3})	4, 1.617	4, 1.695	4, 1.492	2, 1.532	1, 1.443
2 Θ range (°)	3.12 to 27.50	3.24 to 27.51	3.08 to 27.50	3.26 to 27.51	3.08 to 27.50
Cryst size (mm^3)	0.4x0.3x0.2	0.5x 0.4 x 0.3	0.3x0.2x 0.15	0.3x0.3x0.15	0.5x0.3x0.04
no. of rflns collected	21995	9384	12846	23854	12902
no. of indep rflns / R_{int}	2074 / 0.2421	3358/0.0633	2579/0.1349	6634/0.1251	6892/0.0322
no. of data/restraints/params	2074/0/160	3358/0/0.0678	2579/0/171	6634/0/444	6892/0/435
R_1/wR_2 (I>2σ(I))^a	0.0537/0.1133	0.0335/0.0678	0.0514/0.1080	0.0574/0.1075	0.0361/ 0.0721
R_1/wR_2(all data)^a	0.0995/0.1410	0.0731/0.0770	0.1176/0.1417	0.1197/ 0.1351	0.0812/0.0874
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Ä$^{-3}$)	0.617/ -0.806	0.516/-0.676	0.692/-0.583	0.491/-0.943	0.459/-0.288
GOF (on F^2)^a	1.134	1.008	1.079	1.093	0.850

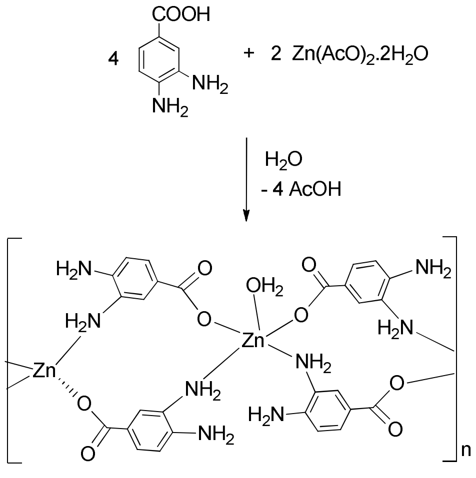
^{a} $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$

Table 2. Data collection details

Compound	1	2	3	4	5
Number of frames	223	133	168	126	269
Total time of exposure (min)	130.6	29.3	68.6	82.1	139.5
Exposure time per frame (s)	34	10	22	38	30
Scan type	φ/ω	φ/ω	φ/ω	φ/ω	φ/ω
scan-width	1.7°	2°	1.5°	1.9°	2°

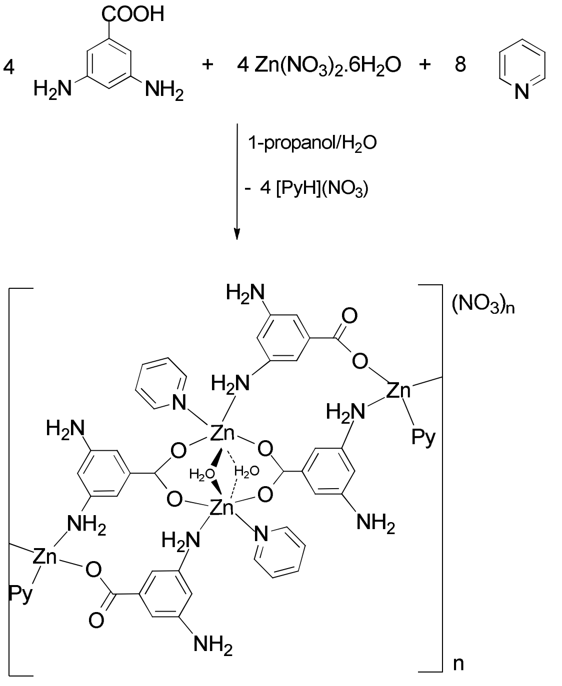
Results and Discussion

The reaction of $Zn(AcO)_2{\cdot}2H_2O$ and 3,4-dabaH led to the formation of the derivative $[Zn(3,4\text{-daba})_2(H_2O)]_n$ (**1**) that was isolated as brown crystals and its structure determined by a single crystal XRD study. As shown in scheme 1, in this compound, the 3,4-diaminobenzoate (3,4-daba) acts as connector. One of its amino substituents remains uncoordinated (see structural discussion below). In this case, the acetate moiety from the precursor could be considered the deprotonating agent to generate the carboxylate species.



1

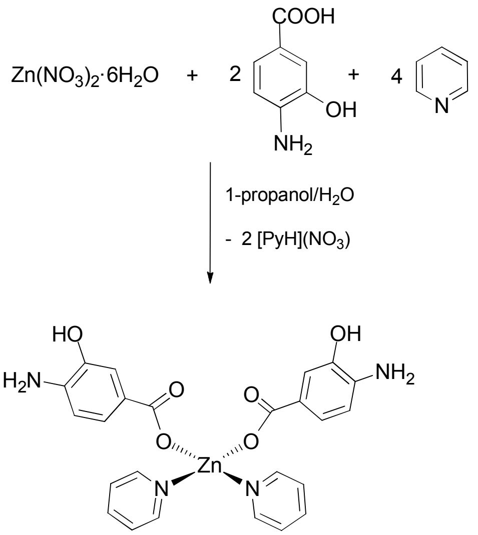
Scheme 1. Synthesis of $[Zn(3,4\text{-daba})_2(H_2O)]_n$ (**1**).



2

Scheme 2. Synthesis of $\{[Zn(3,5\text{-daba})(py)(H_2O)](NO_3)\}_n$ (**2**).

We performed the reaction with 3,5-diaminecarboxilic acid (3,5-dabaH) in the same conditions, but it was not possible to isolate the coordination polymer isostructural to **1**. However, if $Zn(NO_3)_2{\cdot}6H_2O$ and pyridine were used, as metal precursor and base respectively, the 1D structure $\{[Zn(3,5\text{-daba})(py)(H_2O)](NO_3)\}_n$ (**2**) was generated (scheme 2), as shown by a single crystal XRD study. In this reaction, the role of pyridine as the deprotonating agent was confirmed since the salt $[PyH](NO_3)$ could be isolated from the mother liquor. The pyridine also acts as a ligand blocking one of the coordination positions of the metal. The presence of the nitrate is essential as this coordination polymer is cationic and the nitrates are incorporated in the structure. Again, in this derivative, there is one amino group uncoordinated that could be used for further functionalization reactions.



3

Scheme 3. Synthesis of $[Zn(4,3\text{-ahba})_2(py)_2]$ (**3**)

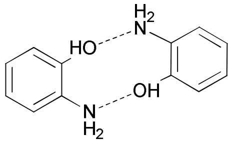
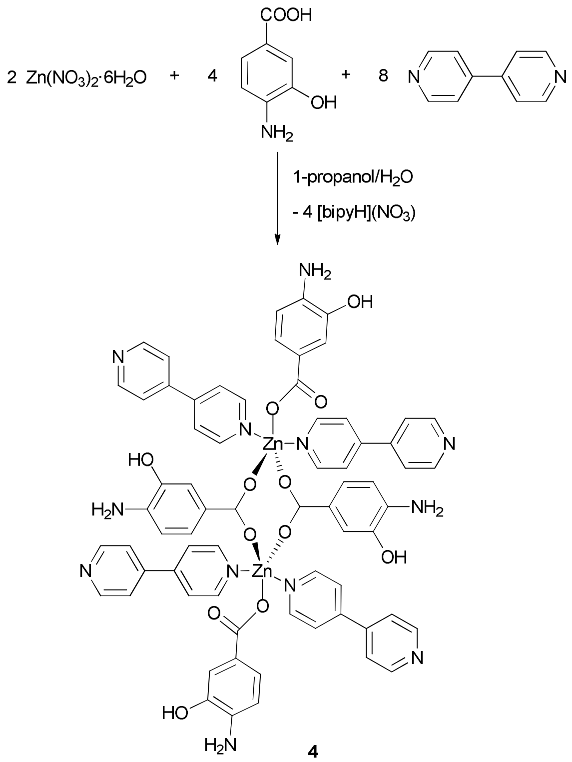


Figure 2. Hydrogen bonding (HB) motif present in **3**.

In our aim of achieving a coordination polymer with a free hydroxyl group, we moved then to check the reaction with an amino-hydroxy benzoic acid. When 3-amino-4-hydroxycarboxilic acid (3,4-ahbaH) was used, no compound could be isolated. However it was possible to obtain derivative **3** if 4-amino-3-hydroxybenzoic acid (4,3-ahbaH) was the ligand precursor. In this case, following the same working conditions as for **2**, the result is very different since the isolated species is the monometallic complex $[Zn(4,3\text{-ahba})_2(py)_2]$ (**3**) where the zinc is bonded to two pyridines and two 4,3-ahba ligands (scheme 3), as determined by a single crystal XRD study. The presence of a strong *synthon* between the hydroxyl group of one ligand and an amine group from an adjacent molecule (figure 2) seems to block the coordination ability of the amino group.

Compound **3** can also be isolated from the mother liquor, and the result is the same if the metal precursor is zinc acetate or zinc nitrate.

Aiming to attain a polymeric structure bearing this amino-hydroxyl carboxylate ligand we used 4,4'-bipyridine as co-ligand since it is frequently applied as a spacer to get extended structures.[22] So we performed the reaction of $Zn(NO_3)_2{\cdot}6H_2O$, 4,3-ahbaH and 4,4'-bipyridine using the same working conditions as for **2** expecting to obtain a one dimensional chain. As a result we could isolate a crystalline orange solid, corresponding to compound **4**.



4

Scheme 4. Synthesis of $[Zn(bipy)_2(4,3\text{-ahba})_2]$ (**4**)

Surprisingly, **4** is a discrete molecule, as shown by the single crystal XRD study of the crystals (scheme 4). In this bimetallic derivative the bipy acts as a monodentated ligand. Again, the hydroxyl group is involved in a strong *synthon*. In this case the pyridine group is a stronger base than the uncoordinated amine and the hydroxyl group prefers to establish the hydrogen bonding interaction with the bipy ligand (figure 3). Probably the presence of this interaction between the nitrogen and the hydroxyl group is the reason why an extended structure is not formed.

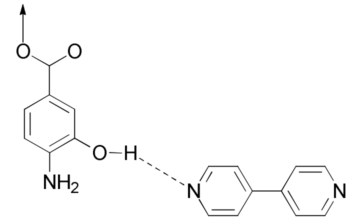


Figure 3. Hydrogen bonding (HB) motif present in **4.**

To check that the hydroxyl group is limiting the formation of a network, we performed the reaction in similar conditions but using *p*-aba and bipy as linkers. In this case, without a hydroxyl group to establish hydrogen bonding interactions it was possible to obtain the 1D species $\{[Zn(4\text{-aba})_2(4,4'\text{-bipy})_2]{\cdot}(H_2O)(4,4'\text{-bipy})\}_n$ (**5**).

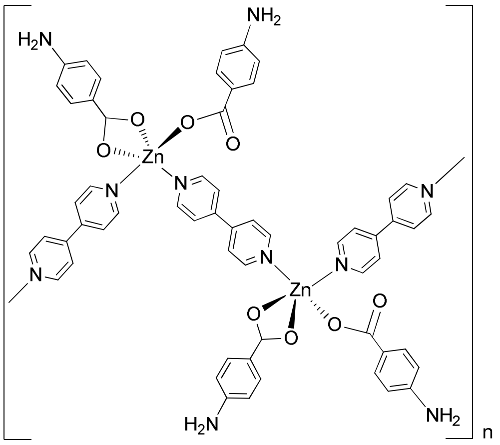


Figure 4. Coordination polymer present in $\{[Zn(4\text{-aba})_2(4,4'\text{-bipy})_2]{\cdot}(H_2O)(4,4'\text{-bipy})\}_n$ (**5**).

Structural Discussion.

For compounds **1-5** it was possible to establish their solid state structure since suitable crystals for single crystal X-ray diffraction were obtained.

The structure for compound **1** is shown in figure 5 and in table 3 a selection of the relevant bond distances and angles is displayed. Compound **1** crystallizes in the orthorhombic P*ccn* space group and presents a 1D chain structure $[Zn(3,4\text{-daba})_2(H_2O)]_n$ where the metal atoms are connected by bridging 3,4-daba linkers.

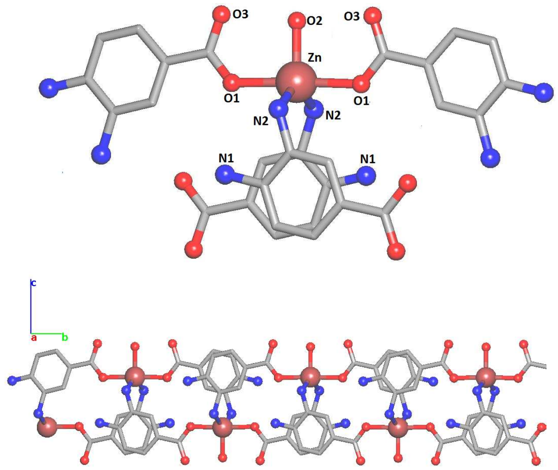


Figure 5. Compound **1** structure. Top: Coordination sphere around the metal. Bottom: View of the 1D chain along *a*.

As shown in figure 5 top, the Zn center is bonded to one water molecule and four 3,4-daba ligands arranged in a distorted trigonal bipyramide coordination sphere. The water molecule and two 3,4-daba ligands coordinated by the amino group in *meta* occupy the equatorial positions. The presence of water as a ligand could be limiting the formation of a structure of higher dimensionality. In the axial positions the remaining two 3,4-daba ligands are placed, coordinated through the carboxylate group in a monodentate fashion with a distance O(1)-Zn of 2.130(3) Å, while the uncoordinated oxygen O(2) is located at 3.326(3) Å from the Zn. The shorter Zn-O distance around the metal corresponds to the oxygen atom from the water molecule, 2.024(3) Å. Within the 3,4-daba ligand, the amino group in *para*-position remains uncoordinated.

The 1D chain is generated along the *b* axis (figure 5, bottom). Each 3,4-daba ligand bridges two Zn atoms, being coordinated to one Zn by the amine group in *meta* and to the other Zn by the carboxylate. It is interesting to note that only two other 1D derivatives have been described with this ligand,[19] [Na(3,4-daba)$(H_2O)_2]_n$ and $[Sn(3,4\text{-daba})_2(C_2H_3)_3]_n$, in the first case the ligand is coordinates by the carboxylate group only and in the tin derivative it is bonded by carboxylate and the amino group in *para* position.

Table 3. Selected bond lengths and angles for compounds **1** and **2**

1		2	
Bond distances(Å)			
Zn(1)-O(2)	2.024(5)	Zn(1)-O(3)	2.0133(16)
Zn(1)-N(2)	2.051(4)	Zn(1)-O(2)	2.0163(17)
Zn(1)-O(1)	2.130(3)	Zn(1)-N(1)	2.086(2)
N(1)-C(7)	1.396(5)	Zn(1)-N(2)	2.178(2)
N(2)-C(2)	1.453(5)	Zn(1)-O(1)#1	2.2366(17)
O(1)-C(1)	1.260(4)	Zn(1)-O(1)	2.3853(18)
O(3)-C(1)	1.271(4)	O(3)-C(6)#1	1.264(3)
C(1)-C(4)#2	1.491(6)	C(6)-O(3)#1	1.264(3)
C(4)-C(1)#3	1.491(6)		
Angles (º)			
O(2)-Zn(1)-N(2)	100.0(2)	O(3)-Zn(1)-O(2)	154.22(7)
N(2)#1-Zn(1)-N(2)	129.3(2)	O(2)-Zn(1)-N(1)	98.75(7)
O(2)-Zn(1)-O(1)	90.5(2)	O(1)-Zn(1)-O(1)#1	94.12(6)
N(2)-Zn(1)-O(1)	86.56(14)	N(1)-Zn(1)-N(2)	90.91(8)
O(1)#1-Zn(1)-O(1)	177.5(1)	O(3)-Zn(1)-N(2)	95.12(7)
C(2)-N(2)-Zn(1)	116.4(3)	Zn(1)-O(1)-Zn(1)#1	85.88(6)
C(1)-O(1)-Zn(1)	128.3(2)		
O(1)-C(1)-O(3)	122.8(4)		

Symmetry transformations used to generate equivalent atoms: for **1** #1 -x+3/2,-y+1/2,z; #2 x-1/2,y-1/2,-z+1; #3 x+1/2,y+1/2,-z+1; for **2** #1 -x+1,-y,-z+2 .

The presence in the asymmetric unit of non-coordinated water molecules between the chains is observed. These water molecules are connected by hydrogen bonding interactions, O(5)-H···O(4) 2.701(4) Å, generating $(H_2O)_3$ supramolecule aggregates (figures 6 and 7), that act as 'gluing factor' in the structure.[23] As such, these entities interact with the coordinated 3,4-daba ligands from neighboring chains and lead the arrangement of the chains into layers. These are also connected through the interaction of the water molecules from the $(H_2O)_3$ unit. As a result, these layers grow nearly perpendicular between them.

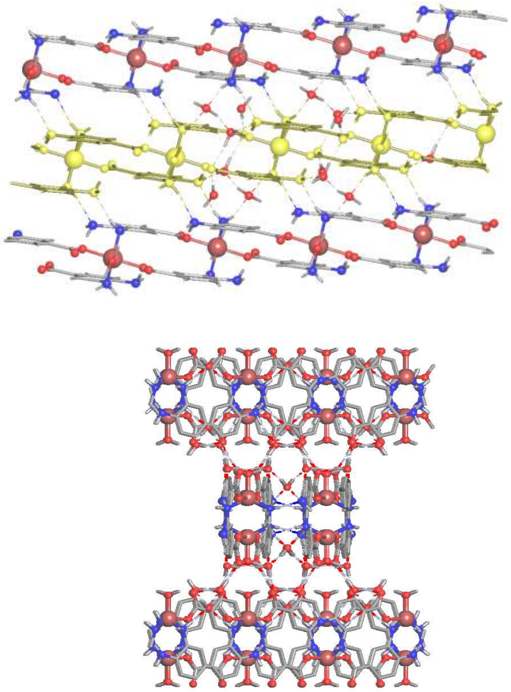


Figure 6. HB in **1** amongst the chains. Top: view along *c*. Bottom: arrangement of the layers

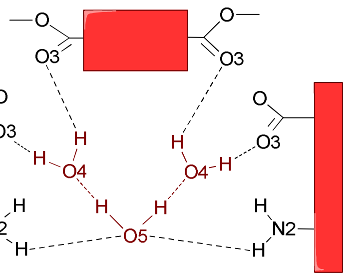


Figure 7. Scheme of the $(H_2O)_3$ supramolecule in **1.**

In the HB interaction N(2)-H···O(5) between the $(H_2O)_3$ supramolecule aggregate and the $[Zn(3,4\text{-daba})_2(H_2O)]_n$ chain, it is interesting to note that the amine group involved is the one coordinated, as expected since those hydrogen atoms will be more acidic than the ones in the uncoordinated NH_2 due to the donation of electron density towards the metal as a result of coordination.

Weak intermolecular interactions are also observed in the crystal packing. Within the chain there is an NH/π interaction between the aromatic ring and the hydrogen from an amine group from the 3,4-daba ligands (figure 1S.a, see SI). The presence of this interaction seems to have a clear influence on the disposition of those ligands as they are placed nearly parallel. There are also π-π stacking interactions between aromatic rings from 3,4-daba ligands from neighboring chains (figure 1S.b, see SI).

Compound **2**, $\{[Zn(3,5\text{-daba})(H_2O)(py)](NO_3)\}_n$, is also a coordination polymer, but in this case the metallic chain is positively charged and the nitrate ion is present in the structure to balance the charge. Compound **2** crystallizes in the monoclinic P2_1/*n* space group. As shown in figure 8, this derivative has a structural unit formed by two zinc atoms bonded by two carboxylate bridges and two bridging water molecules. This central core is constituted by two cycles: one eight-membered formed by two zincs and two carboxylates, and another four membered composed by the metals and the water molecules. Those two rings are placed in planes perpendicular to each other. The carboxylates show a symmetric coordination with similar Zn-O bond values (table 3). However, the water molecules form asymmetric bridges with distances 2.2366(17) and 2.3853(18) Å. The Zn···Zn distance in the Zn_2 unit, 3.151 Å, is within the range 2.9-3.2 Å that is the most frequently observed for Zn_2 units where the metals are bridged by two carboxylate ligands.[15] The octahedral coordination around the zinc atoms is completed by a pyridine and an amine group coming from a third 3,5-daba ligand that also coordinates another structural unit Zn_2 giving a monodimensional chain along *a* (figure 8, bottom). One of the amine groups remains uncoordinated. The presence of the pyridine and water as secondary ligands blocking coordination positions of the metal could be restricting the generation of 2D or 3D structures.

Interestingly this is the first example of a zinc CP with this ligand as linker. Previously this connector has only been reported in six other CPs having Mn, Cd, Co, Pb or Y as metallic centers.[24]

Table 4. Bond lengths and angles for the HB interactions in **1-4**

D-H···A	D···A (Å)	H···A (Å)^a	D-H···A (°)^a
1			
O(4)-H···O(3))#7	2.721(4)	1.784	178.51
N(2)-H···O(5)	2.902(5)	1.910	160.15
O(5)-H···O(4)	2.701(4)	1.770	171.37
O(4)-H···O(3)#8	2.838(12)	1.938	160.08
2			
O(1)-H···N(3)	2.792(3)	1.879	163.85
O(1)-H···O(42)	2.723(2)	1.787	174.92
N(2)-H···O(42)	3.030(2)	2.035	161.77
N(2)-H···O(43)	2.989(3)	1.960	175.95
N(3)-H···O(43)	3.126(3)	2.098	175.33
3			
O(3)-H ··O(2)	2.662(4)	1.730	171.87
N(1)-H ··O(3)	3.178(5)	2.379	133.59
4			
O(5)-H···N(8)	2.760(5)	1.843	165.00
O(6)-H···N(16)	2.758(5)	1.825	172.75
N(4)- H···O(4)	3.018(5)	2.030	159.93

^{a} Normalized values.[25] Symmetry transformations used to generate equivalent atoms: #7 x+3/2, y+1, z-1/2; #8 –x+1,-y+1,-z+1

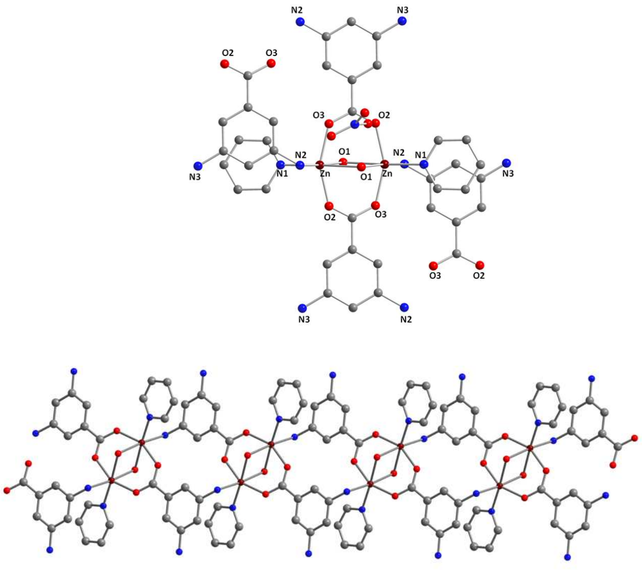


Figure 8. Compound **2** structure. Top: Coordination sphere around the metal. Bottom: View of the 1D chain, nitrate ions are omitted for clarity.

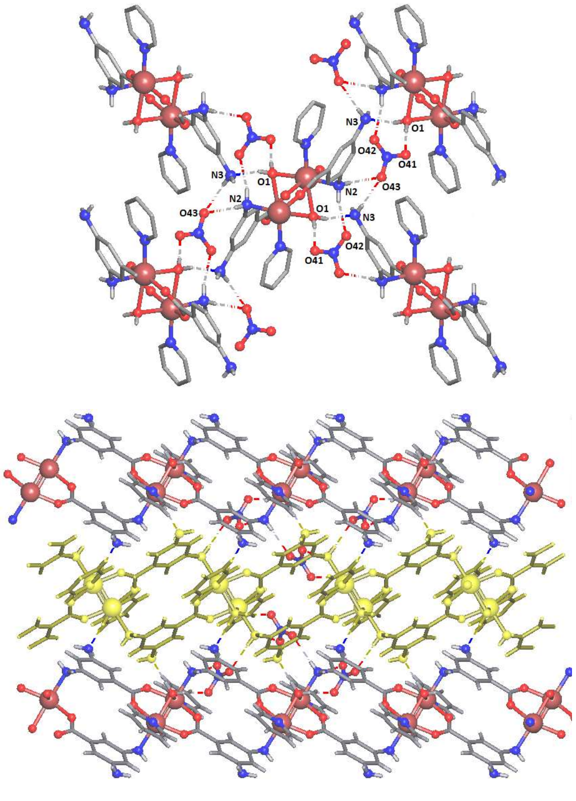


Figure 9. Top: HB interactions in the crystal packing for **2.** Bottom: arrangement of the chains.

The nitrate NO_3^- anions are placed amongst the chains and interact through HB interactions with coordinated amine groups from two different chains, and also with the water ligand. Figure

9 shows the tridimensional arrangement of the chains that is directed by these HB interactions and the one established between the uncoordinated amine group from one chain and the water ligand from an adjacent one, O(1)-H···N(3) 2.792(3) Å.

Within the chains, the pyridine ring and the aryl group of the 3,5-daba ligand are almost parallel with a dihedral angle of 11.25(4)º, (figure 2S.a, see SI). A weak π–π staking interaction is observed that is reinforced by the presence of NH/π interactions between the uncoordinated amine group and the pyridine ring. These kinds of weak interactions, π-π stacking, CH/π and NH/π, also exist in the chain packing amongst the pyridine rings and the aromatic rings from the 3,5-daba ligands (figure 2S.b, see SI).

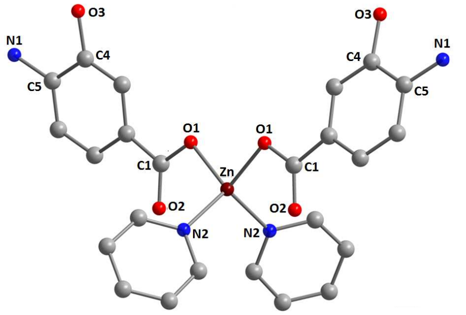


Figure 10. Compound **3** structure.

The structural analysis for **3** evidenced that is a mononuclear derivative where the metal is coordinated to two pyridine ligands and two 4-amino-3-hydroxyl-benzoates in a distorted tetrahedral environment (figure 10). In this case the carboxylate functionality shows a monodentate coordination. The Zn-O distance is shorter in this compound than in **2** as it would be expected since in **3** the ligand is monodentated. Interestingly there are no other examples of complexes with this ligand coordinated. In a CSD search[15] only one other compound appears where the non-deprotonated acid (4,3-ahbaH) is coordinated to the metal by the amine group.[26]

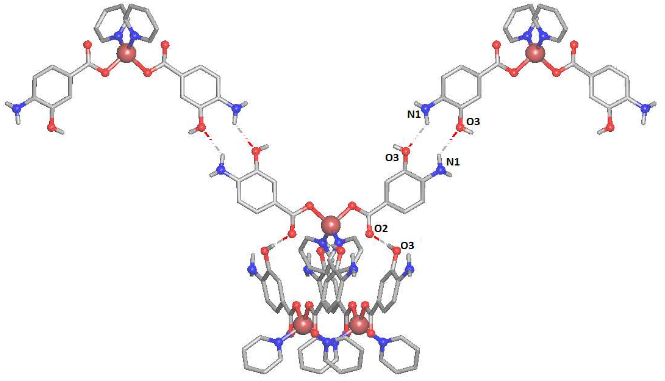


Figure 11. HB network in [Zn(4,3-ahba)$_2$(py)] (**3**). Hydrogen atoms not involved in the HB are omitted for clarity

In the packing a strong *synthon* is observed (figures 2 and 11) between the hydroxyl and amine groups of two 4,3-ahba ligands from two adjacent molecules. The presence of the hydroxyl functionality leads to the generation of this strong N-H···O interaction that does not happen when only amine groups were present. This interaction probably is hampering the possible coordination to another zinc center by these functional groups, obstructing the formation of an extended structure as in **1** or **2**. The hydroxyl is also involved in another interaction with the oxygen from the uncoordinated carbonyl group in the carboxylate moiety, O(3)-H···O(2) 2.662(4) Å.

Table 5. Selected bond lengths and angles for compounds **3** and **4**

3		4	
Bond distances(Å)			
Zn(1)-O(1) Zn(1)-N(2) O(1)-C(1) O(2)-C(1) N(2)-C(12) N(2)-C(8)	1.973(3) 2.030(3) 1.280(5) 1.252(4) 1.331(5) 1.331(5)	Zn(1)-O(1) Zn(1)-O(2) Zn(1)-O(3) Zn(1)-N(3) Zn(1)-N(15)	2.006(3) 1.967(3) 1.955(3) 2.174(4) 2.264(3)
Angles (º)			
O(1)#1-Zn(1)-O(1) O(1)-Zn(1)-N(2) N(2)#1-Zn(1)-N(2) C(1)-O(1)-Zn(1) C(12)-N(2)-Zn(1) C(8)-N(2)-Zn(1) O(2)-C(1)-O(1)	97.31(15) 112.72(13) 111.24(19) 110.2(2) 120.9(3) 121.2(3) 122.2(4)	O(1)-Zn(1)-O(2) O(1)-Zn(1)-O(3) O(2)-Zn(1)-O(3) N(3)-Zn(1)-N(15) O(3)-Zn(1)-N(15) O(2)-Zn(1)-N(3)	137.66(12) 105.37(12) 116.21(12) 171.46(13) 82.92(12) 94.17(12)

Symmetry transformations used to generate equivalent atoms: for **3** #1 -x,y,-z+1/2.

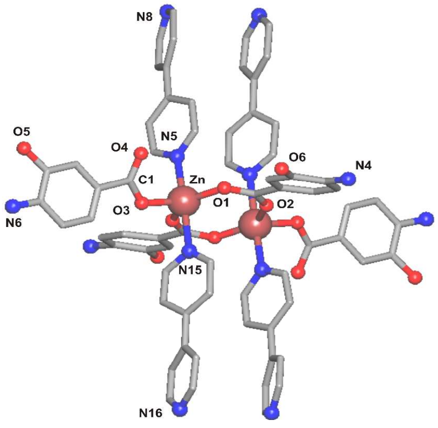


Figure 12. Compound **4** structure.

As stated previously, the structural determination for compound **4** showed its discrete nature (figure 12). This centrosymmetric dinuclear derivative crystallizes in the monoclinic P2$_1$/*n* space group. Both zinc atoms show a distorted bipyramidal trigonal geometry. The axial positions are occupied by nitrogen atoms from the bipy ligands. The equatorial plane is defined by three Zn-O bonds, one coming from a 4,3-ahba ligand coordinated as monodentate and the other two from two bridging carboxylate ligands, so two different coordination modes are observed for the 4,3-ahba ligand. The central core of the compound is an eight membered ring formed by two zincs and two carboxylate bridging groups. This bridge is fairly symmetrical with distances 2.006(3) and 1.967(3) Å. For the monodentade carboxylate ligand the Zn-O3 distance is slightly shorter, 1.955(3) Å. In this case the distance Zn···Zn is 3.654 Å, longer than in **2**, the shorter Zn···Zn distance observed in **2** could be due to the presence of the additional water bridging ligands.

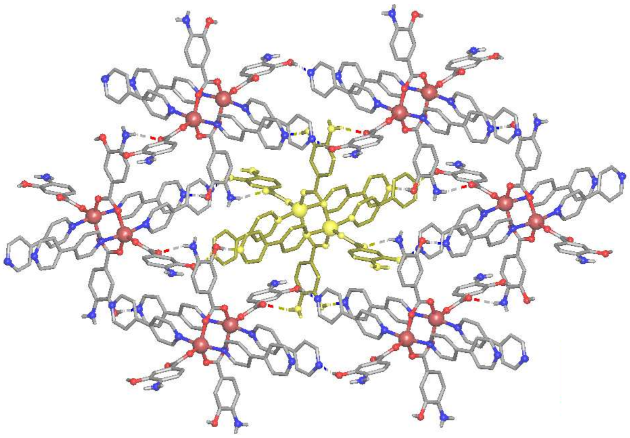


Figure 13. Crystal packing for **4** showing HB interactions.

There is one nitrogen atom uncoordinated in each bipy ligand and the chain growth could be expected to occur through that atom. However, the hydroxide groups from the 4,3-ahba ligand in an adjacent molecule, establish hydrogen bonding interactions with those nitrogen atoms obstructing the generation of an extended structure (figures 3 and 13). Another HB interaction is also observed between the amine group from one bridging ligand and the uncoordinated carbonyl group from a monodentated 4,3-ahba ligand, N(4)H···O(4) 3.018(5) Å.

Finally, the formation of compound **5** $\{[Zn(4\text{-}aba)_2(4,4'\text{-}bipy)_2]\cdot(H_2O)(4,4'\text{-}bipy)\}_n$ proves that the lack of a functionality such as hydroxyl able to generate strong HB interactions, allows the formation of extended structures. As shown in figure 14 this compound is formed by a coordination polymer where the zinc centres are linked by bipy ligands. The coordination polymer present in the structure, $[Zn(4\text{-}aba)_2(4,4'\text{-}bipy)_2]_n$ has been previously described.[27] In **5**, the presence of additional 4,4'-bipy molecules as guests is observed. These guest molecules interact with uncoordinated water molecules generating a supramolecular aggregates $\{(4,4'\text{-}bipy)_2(H_2O)\}$ through N···HO interactions, that are placed in the channels generated from the piling of the different layers of $[Zn(4\text{-}aba)_2(4,4'\text{-}bipy)_2]_n$ chains (figure 14).

In this compound, it is interesting to note the different torsion angles between the free 4,4'-bipy and the ones coordinated. As such, when coordinated both aromatic rings are forced to be nearly co-planar, however, the free 4,4'-bipy ligands present show an angle between the rings of 40.95º.

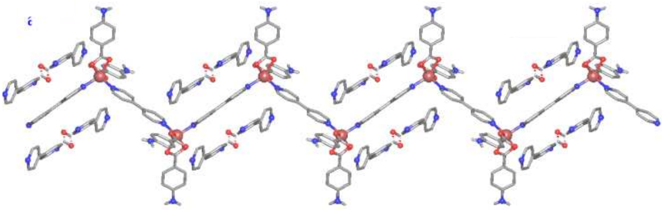


Figure 14. Compound **5** structure

Studies on the coordination ability of the dangling amino groups in **1** and **2** towards arene-Ru(II) fragments are ongoing.

Conclusions

We have explored aminobenzoate ligands showing functional groups in *meta* and/or *para* positions. This work has allowed us to isolate four new compounds of diverse dimensionality, $[Zn(3,4\text{-}daba)_2(H_2O)]_n$ (**1**), $\{[Zn(3,5\text{-}daba)(py)(OH_2)](NO_3)\}_n$ (**2**), $[Zn(4,3\text{-}ahba)_2(Py)_2]$ (**3**) and $[Zn(bipy)_2(4,3\text{-}ahba)_2]_2$ (**4**). Derivatives **1** and **2** present extended structures with uncoordinated amine groups, demonstrating that the diaminobenzoic acids are appropriate ligand precursors for the generation of coordination polymers with non-coordinated amine groups. However in our attempt to obtain hydroxyl tagged species, we observed that the presence of the OH group hampers the possibility of generation of extended structures due to the formation of strong intermolecular interaction motifs.

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Notes and references

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Functionalized aminocarboxylate moieties as linkers for coordination polymers: Influence of the substituents in the dimensionality of the final structure.

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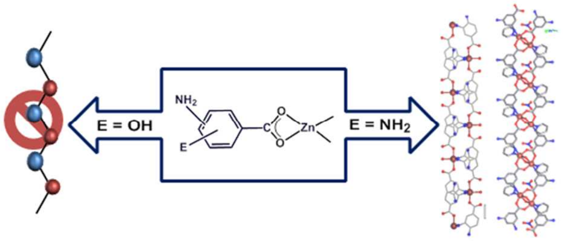

The OH group in the ring hampers the generation of CPs due to the formation of strong intermolecular interaction motifs