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Influence of the metal salt on the self-assembly of isophthaloylbis- β -alanine and Cu(II) ion



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1. Introduction

Amino acids held together via amide bonds to form peptides and proteins serve vital biological functions [1], however in recent years such biomolecules have emerged as building blocks for constructing nanoporous Coordination Polymers (CPs) and Metal Organic Frameworks (MOFs) [2]. This class of ligands presents multiple possible coordination modes and it is also possible to form H-bonds through their non-coordinating heteroatoms. For example, the Fe^{III} gallate, fumarate or muconate MOFs show either rigid small pore structures or structures built from a highly flexible porous matrix [3]. In addition, porous zinc dipeptide based MOFs exhibiting flexible frameworks capable of accommodating CO₂ have also been reported [4].

On the other hand, particular attention has been paid to utilizing ligands based on amino acids attached to aromatic or aliphatic backbones. For example, N-protected amino acids have been extensively used to form complexes in order to better understand the active site of biological systems [5]. Furthermore, several metal coordination compounds, derived from reduced Schiff base ligands, obtained by reducing the C=N bond in the Schiff bases formed by the condensation of aldehyde and various natural/unnatural amino

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ABSTRACT

The initial employment of the new pseudopeptidic ligand isophthaloylbis- β -alanine (H₂IBbA, H₂L) with Cu^{II} ion affords a one dimensional (1D) [Cu₂L₂(H₂O)(CH₃OH)]·2H₂O·CH₃OH (1) and a two dimensional (2D) [Cu₂L₂(H₂O)₄]·6H₂O (2) compound, respectively, illustrating the important influence of the metal salt and the solvent system used in determining the motif of the final product. Infrared spectroscopy, thermal, adsorption and theoretical studies of these compounds are also discussed.

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acids, have been reported and show interesting properties [6]. In this direction, we and others have shown that placing amino acid groups on aromatic scaffolds yields pseudopeptidic ligands which in turn can be used along with various metal centres to synthesize CPs [7,8]. From the structural point of view, the reactions of terephthaloylbisglycine (H₂TBG, Scheme 1 upper) and isophthaloylbisglycine (H₂IBG, Scheme 1 middle) along with Cu^{II} ion results in a non-porous 2-fold interpenetrated three dimensional (3D) CP formulated as [Cu(µ-TBG)(µ-H₂O)(H₂O)₂] 2(H₂O) [7a,b] and a 2D CP formulated as $[Cu(\mu-IBG)(\mu-H_2O)(H_2O)_2]\cdot 2(H_2O)$ [7d], respectively. In both cases, the product has the same molecular formula and each Cu^{II} centre has the same coordination environment but the different positions of the two (CONHCH₂COO) units in the aromatic ring result in compounds with different dimensionality. From the crystal engineering point of view, such pseudopeptidic ligands are of great interest because they can give access to the synthesis of pseudo polymorphs [7c,e] as well to $2D + 2D \rightarrow 3D$ parallel polycatenated structures [7e].

2. Experimental

2.1. Materials and instrumentation

All chemicals and solvents used for synthesis were obtained from commercial sources and used as received without further purification. All reactions were carried out under aerobic





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conditions. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AMX 500 MHz spectrometer. All spectra were recorded using commercially available d⁶-DMSO or D₂O (Aldrich) of 99.6% isotopic purity or better and referenced to a residual solvent. The elemental analyses (C, H and N) were carried out at the Institute of Nanotechnology, Karlsruhe Institute of Technology, using an ElementarVario EL analyzer. Fourier transform IR spectra (4000–400 cm⁻¹) were measured on a Perkin–Elmer Spectrum GX spectrometer with samples prepared as KBr discs. Thermogravimetric analysis (TGA) curves were measured using a Netzsch STA 409C Thermal Analyzer under nitrogen flow (30 mL min⁻¹) at a scan rate of 5 °C min⁻¹ from 25 to 800 °C.

2.2. Synthesis of the compounds

2.2.1. Synthesis of isophthaloyl-bis- β -alanine (H₂L)

β-Alanine (7.127 g, 0.080 mol) and NaOH (4.80 g, 0.120 mol) were dissolved in water (50 mL) with stirring in a round-bottomed flask in an ice bath. After the solution cooled to below 10 °C, a solution of isophthaloylchloride (8.12 g, 0.040 mol) dissolved in toluene (50 mL) was added drop wise. The reaction mixture was stirred for one hour, after which the aqueous phase was separated from the organic phase and collected. The aqueous phase was acidified with 35% HCl until the pH was approximately 1. The white product was collected by vacuum filtration and dried in a vacuum oven overnight at 50 °C. Yield: 12.33 g, 100%. Anal. Calc. for C14H16N2O6 (found): C, 54.54 (54.22); H, 5.23 (5.20); N, 9.09 (8.98)%. ¹H NMR (ppm): 2.55 (t, 4H), 3.48 (m, 4H), 7.55 (t, 1H), 7.98 (dd, 2H), 8.40 (s, 1H) 8.79 (*t*, 2H), 12.32 (*s*, 2H). ¹³C NMR (ppm): 33.70, 35.58, 126.14, 128.29, 129.76, 134.39, 165.79, 172.81. Selected IR data (KBr disc, cm⁻¹): 3345, 3080, 2956, 2662, 2531, 1727, 1630, 1581, 1545, 1481, 1433, 1400, 1381, 1371, 1313, 1279, 1202, 1082, 1037, 1000, 932, 914, 879, 858, 826, 798, 729, 706, 686.

2.2.2. Synthesis of $[Cu_2L_2(H_2O)(CH_3OH)] \cdot 2H_2O \cdot CH_3OH(1)$

 H_2L (154 mg, 0.500 mmol) and Et_3N (69 µl, 0.500 mmol) were dissolved in MeOH (30 mL) with stirring. $Cu(OAc)_2 H_2O$ (100 mg, 0.500 mmol) was dissolved in H_2O (20 mL) and then added to the methanolic solution. The final solution was stirred at room



Scheme 1. Pseudopeptidic ligands used in previous and present works.

temperature for 30 min and then filtered and left undisturbed. Slow evaporation yielded green crystals after almost 3 weeks. The crystals were collected by filtration and washed with Et₂O. Yield: 190 mg, 92% based on Cu. *Anal.* Calc. for $C_{29}H_{38}Cu_2N_4O_{16}$ (found): C, 42.18 (42.04); H, 4.64 (4.78); N, 6.79 (6.71)%. Selected IR data (KBr disc, cm⁻¹): 3468, 3389, 2959, 1656, 1605, 1540, 1475, 1445, 1424, 1319, 1281, 1076, 715, 683.

2.2.3. Synthesis of $[Cu_2L_2(H_2O)_4] \cdot 6H_2O(2)$

H₂L (154 mg, 0.500 mmol) and Et₃N (69 µl, 0.500 mmol) were dissolved in H₂O (40 mL) with stirring. Cu(NO₃)₂ 2.5 H₂O (116 mg, 0.500 mmol) was dissolved in MeOH (10 mL) and then added to the aqueous solution. The final solution was stirred at room temperature for 30 min and then filtered and left undisturbed. Slow evaporation yielded light blue crystals after almost 2 weeks. The crystals were collected by filtration and washed with Et₂O. Yield: 210 mg, 92% based on Cu. *Anal.* Calc. for C₂₈H₄₈Cu₂N₄O₂₂ (found): C, 36.56 (36.34); H, 5.26 (5.38); N, 6.09 (6.11)%. Selected IR data (KBr disc, cm⁻¹): 3399, 3286, 1662, 1626, 1574, 1433, 1407, 1316, 1295, 1262, 1205, 1080, 727.

2.3. Computational details

All calculations were performed using the GAUSSIAN09 suite of programs [9] employing the M05-2X [10a] functional combined with the Def2-TZVP basis set [10b] for copper and the Pople's 6-31G(d,p) basis set for the non metal atoms. Single point calculations were performed on the building blocks of the 1D and 2D CPs using the geometries determined by X-ray crystallography. The geometry of the dianionic pseudopeptidic isophthaloyl-bis- β alanine ligand (IBba²⁻) was fully optimized at the M05-2X/ 6-31G(d,p) level in aqueous solution employing the universal continuum solvation model based on solute electron density called SMD [11] starting from both the *svn*- and *anti*-conformations of the IBba²⁻ ligand. The interconversion of the *svn*- and *anti*-conformations of the IBba²⁻ ligand in aqueous solution was investigated by calculating the potential energy surface for the adiabatic rotation of the β -alanine moiety around the C–C bond employing the M05-2X/6-31G(d,p) computational protocol. The natural bond orbital (NBO) population analysis was performed using Weinhold's methodology [12,13]. The ELF (Electron Localization Function) plots were obtained by employing the Multiwfn software version 2.2.1 [14].

2.4. X-ray crystallographic study

Data for 1-2 were collected at 180 K on a Stoe IPDS II area detector diffractometer using graphite-monochromated Mo Ka radiation. Semi-empirical absorption corrections were applied using XPREP in SHELXTL [15a]. The structures were solved using direct methods, followed by a full-matrix least-squares refinement against F^2 (all data) using SHELXTL [15a]. Anisotropic refinement was used for all ordered non-hydrogen atoms; organic hydrogen atoms were placed in calculated positions, while atomic coordinates of hydroxo hydrogen and amine hydrogen atoms were either placed in calculated positions or located from the difference Fourier map and then constrained to ride on their parent atom with $U_{iso} = 1.5 U_{eq}$ (parent atom). Hydrogen atoms of the water of crystallization and methanol molecules in the structure of 1 could not be located from difference Fourier maps and their positions were calculated with CALCOH implemented into WinGX [15b]. The crystal data and the parameters of the structure refinement are listed in Table 1.

3. Results and discussion

3.1. Synthesis

Both compounds were prepared under normal atmospheric conditions in aqueous-methanolic solutions. Although the preparation of the two compounds looks quite straightforward, the isolation of pure and homogeneous samples, especially for **1** (Fig. S1), proved rather tedious.

We started our synthetic attempts utilizing 1:1 aqueous:methanolic solutions of Cu^{II} salts and the pseudopeptidic ligand. In most of the experiments, light blue microcrystalline solids were isolated which eventually proved to be compound 2 (Fig. S2). Using different Cu^{II} salts such as nitrate, chloride, perchlorate, sulfate and freshly prepared hydroxide in the reaction results in the isolation of compound **2**. When $Cu(OAc)_2 H_2O$ was used as Cu^{II} source, we isolated a mixture of green and light blue crystals which eventually proved to correspond to compounds 1 and 2, respectively. Reactions, with an excess either of the metal salt or the ligand, with metal-to-ligand ratio spanning the range 2: 1 to 1: 2, led to the formation of **2** with all the salts except the acetate which led to mixtures of 1 and 2. In order to rationalize the influence of the solvent on the final product and its purity, several experiments were carried out changing solvents and the degree of the solvent hydration. When MeOH was replaced with heavier alcohols (such as EtOH or ⁱPrOH), acetone or DMF we isolated solids formulated as 2 but with different solvation properties. Scanning MeOH:water ratios in the reaction system, we found out that we could increase the amount of the green crystals in the crystalline mixture by increasing the amount of MeOH. We manage to isolate pure **1** (Fig. S1) using a 3:2 MeOH:water system. Compound 1 can be isolated in pure form utilizing MeOH:water ratios up to 5:1. Both coordination polymers are stable and retain their crystallinity in air, but 2 dehydrates easily upon gentle heating or storing in a desiccator.

3.2. Crystal structure description

The green crystals of compound **1** crystallize in the monoclinic space group $P2_1/c$ with Z = 4. The crystal structure of **1** reveals a 1D

Table 1Crystal data and structure refinement for 1 and 2.

strand running along the *b* axis. The asymmetric unit (Fig. 1) of **1** comprises of two Cu^{II} centres, two organic ligands, one ligated water and one ligated methanol molecule, and two water and one methanol as solvent of crystallization. The two Cu^{II} centres possess the well-known paddle - wheel motif and are ligated to four carboxylate groups belonging to four different organic ligands with the axial positions being occupied by one water molecule (on Cu2) and one methanol molecule (on Cu1). Each organic ligand is coordinated to four Cu^{II} centres (coordination mode I, Scheme 2) belonging to two different paddle wheels, while all carboxylate and peptidic groups are planar in trans arrangement. This way the strand extends with alternating rings formed by two paddlewheels and two ligands (Fig. 1). The molecular conformation is also characterized by the $NC_{amido}C_{aryl}C_{aryl}$ torsion angles (see Table 2) which clearly indicate that the planar amide groups are placed in the plane of the benzene ring, resulting in a planar arrangement for the $CH_2NHCO(m-C_6H_4)CONHCH_2$ residue (max deviations from least squares planes are 0.22 Å for N2 in ligand C1-C14 and 0.14 Å for N4 in ligand C15-C28).

The Cu atoms belonging to the same ring are essentially co-planar. Adopting the nomenclature described before [7d], the first ligand (C1–C14) adopts an *atata* conformation while the other ligand (C15–C28) adopts a *btatb* conformation. Alternatively, the metal-atom plane is an approximate mirror plane in the ring or bisects the angle formed by the two ligands planes (122.60°), therefore both ligands can be described as having *atata* conformations. When the solvent molecules are removed, narrow channels appear into the 1D zig–zag strands. The void space is 6.5% of the cell volume (234.1 Å³) as calculated with Platon.

There is an extended hydrogen bonding network stabilizing the crystal structure of **1**. The geometrical characteristics of all H-bonds can be found in Table T1. It is worth noting that all solvent of crystallization are held on the inner side of the 'tube' formed along the 1D strands, while each strand interacts with four neighbouring strands via the amide bond pointing out from the strand, i.e., the two N2–H2N and N4–H4N hydrogen atoms and the two C4–O3 and C18–O9 carbonyl oxygen atoms. The complete H-bond pattern is presented in Fig. 2.

Empirical formula	C20H42CU2N4O17	C20H40CU2N4O22	
Formula weight	857 76	919 78	
T (K)	180(2)	180(2)	
λ (Å)	0.71073	0.71073	
Crystal system	monoclinic	monoclinic	
Space group	P21/c	Pc	
Unit cell dimensions			
a (Å)	16.7550(10)	15.978(3)	
b (Å)	8,7603(5)	7.1089(8)	
c (Å)	29.3760(16)	16.458(3)	
β(°)	123.360(8)	99.110(14)	
$V(Å^3)$	3601.3(4)	1845.8(5)	
Z	4	2	
Calculated density (Mg/m^3)	1.582	1.655	
Absorption coefficient (mm^{-1})	1.262	1.247	
F(000)	1776	956	
Crystal size (mm)	$0.10\times0.08\times0.05$	$0.20\times0.12\times0.07$	
Theta range for data collection (°)	1.66–25.71	1.29-25.72	
Limiting indices	$-20 \leqslant h \leqslant 20, -9 \leqslant k \leqslant 10, -35 \leqslant l \leqslant 35$	$-19 \leqslant h \leqslant 19, -8 \leqslant k \leqslant 8, -19 \leqslant l \leqslant 19$	
Reflections collected/unique	$22595/6780 [R_{int} = 0.1258]$	$22382/6925 [R_{int} = 0.0716]$	
Completeness to θ = 25.00	99.8%	99.9%	
Maximum and minimum transmission	0.9396 and 0.8842	0.9178 and 0.7886	
Refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F^2	
Data/restraints/parameters	6780/12/495	6925/26/530	
Goodness-of-fit on F^2	0.943	0.952	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0774, wR_2 = 0.1898$	$R_1 = 0.0386, wR_2 = 0.0673$	
R indices (all data)	$R_1 = 0.1527, wR_2 = 0.2143$	$R_1 = 0.0563, wR_2 = 0.0706$	
Largest difference peak and hole ($e A^{-3}$)	2.470 and -0.831	0.528 and -0.477	



Fig. 1. (Upper) the asymmetric unit of **1**, extended to show the coordination of the ligand and the coordination sphere of the metal ions. (Middle) perspective view of the strand in **1**, running parallel to *b* and (lower) down to *ac* plane. CH hydrogen atoms and solvent molecules have been omitted for clarity.

The blue crystals of compound **2** crystallize in a monoclinic space group Pc with Z = 2. The crystal structure of **2** is composed



Scheme 2. Coordination modes found in compounds 1 (mode I) and 2 (mode II).

Table 2 Selected torsion angles (°) for compounds 1 and 2.

1		2	
N1C4C5C10	177.4(9)	N1C4C5C10	29.5(16)
N2C11C7C8	-11.5(14)	N2C11C7C8	39.3(15)
N3C18C19C24	178.8(8)	N3C18C19C24	36.6(15)
N4C25C21C22	4.5(12)	N4C25C21C22	27.6(15)

of Cu^{II} dimers (Cu...Cu 3.407 Å) linked by the organic ligands into an infinite 2D network. The asymmetric unit of **2** consists of two Cu^{II} centres, two organic ligands, four ligated and six water of crystallization molecules. Both Cu^{II} centres are five coordinate possessing a square pyramidal geometry; O7, O13, O14, O11' and O2, O15, O16, O5' form the basal planes for Cu1 and Cu2, respectively, while O2 and O11' occupy the axial positions for Cu1 (2.366(3) Å) and Cu2 (2.402(3) Å), respectively. Thus, the two Cu^{II} centres are only bridged through two carboxylate oxygen atoms O2 and O11' (Cu1–O2–Cu2 104.07(13)° and Cu1–O11'–Cu2 102.21(12)°). Analysis of the shape determining angles using the approach of Addison, Reedijk et al. [16] yields a value for trigonality index, *s*, of 0.17 for Cu1 and 0.16 for Cu2 suggesting square pyramidal geometries (*s* = 0 and 1 for perfect *sp* and *tbp* geometries, respectively).

Interestingly, this motif, i.e., a dimer formed by two five coordinated aqua carboxylate complexes sharing an edge, is unexpectedly rare in transition metal chemistry. A search in CSD [17] revealed only eight examples; one Mn^{II} [18a], two Zn^{II} [18b,c] and five Cu^{II} complexes [18d–h] and none of them in a coordination polymer, therefore it can be characterized as a new SBU in MOF chemistry.

Each organic ligand is coordinated to three Cu^{II} centres (coordination mode II, Scheme 2), while all carboxylate and peptidic groups are planar. The NC_{carbnyl}C_{aryl}C_{aryl} torsion angles (see Table 2) clearly indicate that the planar amide groups are displaced out the plane of the benzene ring which is in contrast to compound **1**. The reason for this non-planarity appears to be the strong hydrogen bonds between the peptide moieties of adjacent ligands (detailed geometrical characteristics are presented in Table T4). Moreover the first ligand (C1–C14) adopts an *atsta* conformation while the other ligand (C15–C28) adopts a *btstb* conformation [7d]. The Cu^{II} dimers are linked by the organic ligands to form a 2D coordination polymer (Fig. 3). From the topological point of view, considering each metal centre and each ligand as a node then the 2D net possessing a **fes** topology is formed while considering each Cu^{II} dimer as a node then an **sql** network is formed.

There is an extended network of hydrogen bonds which provides extra stabilizing interactions. The asymmetric unit of **2** also



Fig. 2. A packing diagram of 1, indicating the intra- and inter-chain H-bonding interactions stabilizing the crystal structure, shown down to *ac* plane. CH hydrogen atoms have been omitted for clarity.

contains six water of crystallization molecules which are located between the layers and held in the architecture with H-bonds. Generally, all the H-bonds of the structure can be separated into three distinct groups: (a) the intra-layer H-bonds, which include two of the amide moieties {N2-H2N···O10 and N3-H3N···O3 (x, y+1, z) and two coordinated water molecules which are H-bonded to the coordinated carboxylates {014-H141...01 $(x, y+1, z), 014-H142\cdots O6(x-1, -y+1, z+1/2), 015-$ H151...O8(x, y = 1, z) and O15-H152...O12(x = 1, -y, z + 1/2) as donors; (b) the inter-layer H-bonds, which include the other two amide moieties which are H-bonded as donors to a carboxylate group {N1–H1N···O8(x, -y + 1, z – 1/2) and to a coordinated water molecule {N4–H4N···O16(x + 1, y + 1, z)}; and (c) the water of crystallization molecule H-bonds. The latter water molecules act as bridges between the layers reinforcing the overall architecture. The amide NH H-bonds are depicted in Fig. 4. The interlayer H-bonds {i.e. N1-H1N···O8(x, -y + 1, z - 1/2) and {N4-H4N··· O16(x + 1, y + 1, z) are responsible for the polarity of the space group (Pc) for **2**, since they are pointing to the same direction parallel to *c* axis [19].

3.3. Thermal and structural studies

The experimental powder XRD patterns of the bulk material of both compounds (Figs. S1 and S2) fit well with the theoretical powder XRD pattern. Thermogravimetric analysis (TGA) was carried out on both compounds (Fig. 5). In compound **1**, the solvent of crystallization was removed step wise; part of the crystallization solvent is removed at 120 °C and 180 °C (calculated 7.93%, experimental 7.38%). In compound **2**, the thermal behaviour differs to that of **1**; all the water molecules were successfully removed in one step at 120 °C (calculated 19.57%, experimental 19.38%). The decomposition of both compounds starts at 220 °C resulting in CuO metal oxide as the final residue according to weight loss calculations.

Having in mind the different thermal behaviour of **1** and **2** and the possibility that these two compounds can be interconverted, several experiments were performed [20]. Samples of both compounds were heated at 150 °C under vacuum, to remove all solvent molecules, and then the desolvated samples were placed in H₂O or MeOH or H₂O/MeOH solutions to check the possibility that **1** can be transformed to **2** or *vise versa* (Figs. S5–S7). The IR data of the desolvated samples indicate that in both compounds the organic molecules retain their initial coordination modes. However, the comparison of the IR data of the initial, heated and resolvated samples (Figs. S6 and S7), indicate that the structural transformation of **1** to **2** or **2** to **1** is impossible. Furthermore, efforts to recrystallize compounds **1** and **2** to form **2** and **1**, respectively, were unsuccessful.

3.4. Theoretical studies

At first we investigated the conformational preference of the dianionic IBbA^{2–} ligand in aqueous solution by optimizing the geometry of the dianion at the M05-2X/6-31G(d,p) level employing the universal continuum solvation model based on solute electron density (SMD) starting from both the *anti-* and *syn*-conformations of the amide carbonyl groups. The optimized equilibrium geometries are shown in Fig. 6.

The IBbA²⁻ ligand with the *anti*-conformation of the carbonyl groups is slightly more stable than that with the *syn*-conformation ($\Delta E = 0.6$ kcal/mol at the M05-2X/6-31G(d,p) level in aqueous



Fig. 3. (Upper) the asymmetric unit of **2**, extended to show the coordination of the ligand and the coordination sphere of the metal ions. CH hydrogen atoms and solvent molecules have been omitted for clarity. Label scheme is complete and the atoms are at the 50% probability level. Symmetry operations to generate equivalent atoms: #1, x - 1, -y + 1, z + 1/2; #2, x - 1, -y, z + 1/2; #3, x + 1, -y, z - 1/2; #4, x + 1, -y + 1, z - 1/2. (Lower) a view of the 2D thick layer formed in **2**, indicating the intra-layer H-bonding interactions stabilizing the crystal structure. CH hydrogen atoms and water of crystallization molecules have been omitted for clarity.



Fig. 4. A packing diagram of 2 shown down to *b* axis. Intra-layer H-bonds are drawn in red while inter-layer in green. CH hydrogen atoms and water of crystallization molecules have been omitted for clarity. (Color online.)



Fig. 5. TGA graphs of compound 1 (orange line) and 2 (blue line). (Color online.)

solution and 1.6 kcal/mol at the M05-2X/6-311+G(d,p) level in vacuum). It is noteworthy that the *syn*-conformation of the IBba²⁻ ligand shown in Fig. 6 was obtained even starting from the geometry of the coordinated IBba²⁻ ligand in **2**. The latter corresponds to a third order saddle point on the potential energy surface, but only 3.2 kcal/mol higher in energy than the global minimum and therefore could be accessible upon coordination with the Cu^{II} metal centres. It is obvious that the two conformers of the IBbA²⁻ ligand coexist in equilibrium in aqueous solution.

The interconversion of the syn- and anti-conformations of the IBbA²⁻ ligand in aqueous solution is characterized by a low rotational barrier (around 5.0 kcal/mol) as shown from the calculated potential energy surface for the adiabatic rotation of the β-alanine moiety around the C-C bond depicted schematically in Fig. 6. It is also noteworthy that both the β -alanine moieties in the crystal structure of 2 are not co-planar with the aromatic benzene ring. In the syn-conformer the OCCO dihedral angle is 79.5° (93.3° in vacuum at the M05-2X/6-311+G(d,p) level), with the C=O groups of the two β -alanine moieties pointing towards opposite directions with respect to the benzene ring. The same holds true in the anti-conformer, see compound **1**, where both the β -alanine moieties are also not co-planar with the aromatic benzene ring; the OCCO dihedral angle is -123.6° (162.7° in vacuum at the M05-2X/6-311+G(d,p) level) and the C=O groups of the two β-alanine substituents point towards opposite directions with respect to the ring plane. In both conformers the carboxyl moieties. C(O)O, acquire negative natural atomic charges of -0.89 |e| and have similar proton affinities estimated to be 361.7 kcal/mol in vacuum at the M05-2X/6-311+G(d,p) level.

The influence of the metal salt on the self-assembly of isophthaloyl-bis- β -alanine and Cu^{II} ions could be explained by considering the substitution reactions that yield compounds **1** and **2**. Cu(OAc)₂ in solid state and in aqueous solution possesses the well-known [Cu(OAc)₂(L)]₂ paddle – wheel motif where the Cu^{II} centres *syn,syn*-bridged by four acetate groups, while the two axial positions are occupied by water and/or methanol ligands [21]. Therefore, compound **1** is the product of substitution of the acetate ligands by the IBbA^{2–} ligand, thus maintaining the paddle – wheel



Fig. 6. Equillibrium geometries of the IBba²⁻ ligand along with the potential energy surface for the adiabatic rotation of the β-alanine moiety around the C–C bond calculated at the M05-2X/6-31G(d,p) level.

structure. Notice that the intermetallic Cu-Cu distance 2.604 Å in 1 is comparable to that of 2.617 Å in the $[Cu(OAc)_2(L)]_2$ dimer. On the other hand, the copper nitrate, chloride, perchlorate and sulfate salts in aqueous solutions exist mainly as square planar $[Cu(H_2O)_4]^{2+}$ and/or octahedral $[Cu(H_2O)_6]^{2+}$ species. Therefore, substitution of the water ligands by the IBba²⁻ ligands yields the five coordinated Cu^{II} in compound **2**. The estimated proton affinities of the $IBba^{2-}$ and acetate ligands in vacuum were found to be 361.7 and 344.5 kcal/mol, respectively, at the M05-2X/ 6-311+G(d,p) level indicating that the IBbA²⁻ ligand is a slightly stronger nucleophile than acetate, thus accounting for the substitution of acetate in the $[Cu_2(OAc)_4(H_2O)_2]$ complex yielding **1**. It is interesting to note that the Cu^{II} atoms acquire lower positive natural atomic charges in the $[Cu_2(OAc)_4(H_2O)_2]$ complex than in **1**, thus reducing the repulsive electrostatic interactions between the Cu^{II} atoms and renders the intermetallic $\mathsf{Cu}\cdots\mathsf{Cu}$ separation distance shorter. It is worth noting that, according to the estimated Wiber Bond Index (WBI) value of 0.08, the covalent intermetallic interactions are negligible.

In order to throw light on the conformational preferences of compounds **1** and **2** we performed single point calculations on the crystal structures of the complexes involving the IBba^{2–} ligands either in the *anti-* or the *syn*-conformation. It was found that compound **1** with the IBbA^{2–} ligands in the *anti-*conformation is more stable (by 15.2 kcal/mol) than the structure with the IBbA^{2–} ligands in the *syn*-conformation in line with experiment. On the other hand compound **2** with the IBbA^{2–} ligands in the *syn*-conformation is more stable (by 5.3 kcal/mol) than the structure with the IBbA^{2–} ligands in the *anti-*conformation is more stable (by 5.3 kcal/mol) than the structure with the IBbA^{2–} ligands in the *anti-*conformation in line with experiment.

To see whether steric interactions are responsible for the conformational preferences in compounds **1** and **2** we truncated the $CH_2CH_2C(O)O$ end of each $IBbA^{2-}$ ligand affording the coordinated $O(O)C(CH_2)_2NHC(O)C_6H_4C(O)NH_2$ ligands. It was found that in compound **1** with the $IBba^{2-}$ ligands in the *anti*-conformation the truncated $CH_2CH_2C(O)O$ end contributes to repulsive steric interactions by 5.3 kcal/mol. Similarly in compound **2** with the $IBba^{2-}$ ligands in the *syn*-conformation the truncated $CH_2CH_2C(O)O$ end contributes to repulsive steric interactions by 9.3 kcal/mol. Thus even with this truncation the conformational observed geometries remain more stable. The repulsive steric interactions in **2** are further corroborated by the energy release (estimated to be 9.6 kcal/mol) that accompanies the complete separation of the two 1D chains of **2**.

3.5. Discussion

In the present study the coordination abilities of the pseudopeptidic ligand H₂IBbA along with various Cu^{II} salts were investigated. The different coordination behaviour of the ligand observed in compounds 1 and 2 can be attributed to the different Cu^{II} starting material and solvent used. This is the first report of this ligand in the literature and therefore, due to the semi-flexibility of the ligand, any prediction for the final product is not valid. A literature survey indicates that β -alanine has been widely employed for the synthesis of finite and infinite structures [22] either being chelated to a metal centre [22e] or being coordinated only through the carboxylic group [22a-d]. Interestingly, N-acetyl- β -alanine (Ac- β -alaH), a ligand which is very close structurally related to H₂IBbA, reacts with freshly prepared Cu(OH)₂ to give a mononuclear compound formulated as $Cu(Ac-\beta-ala)_2 \cdot 2H_2O$, while a recrystallization of the latter gives a dinuclear compound formulated as $[Cu(Ac-\beta-ala)_2 H_2O] \cdot 2H_2O$ possessing a paddle wheel motif [5]. The coordination modes of Ac- β -alaH reported in the latter study are very closely related to the coordination modes of H₂IBbA found in **1** and **2**. This leads to the conclusion that the coordination abilities of the carboxylate group of the N-protected β -alanine moiety are not altered by being incorporated into an aromatic scaffold. In addition, the theoretical studies presented herein indicate that compounds **1** and **2** are the thermodynamically most favourable products; therefore the possibilities of obtaining a large variety of products under specified synthetic conditions are highly restricted. With this in mind, in order to give an explanation of the different coordination modes of the H₂IBbA ligand, we assume that the paddle wheel motif of $[Cu(OAc)_2L]_2$ is retained in the solution and therefore compound **1** is the product of substitution of the acetate ligands by carboxylate groups of the IBbA²⁻ ligand. In this case, the IBbA²⁻ ligand adopts the most favourable anti-conformation as could be substantiated from the theoretical studies. For 2, it is well known that the salts $Cu(NO_3)_2$, $CuCl_2$, $Cu(ClO_4)_2$, $Cu(SO_4)$ in aqueous solutions yield hydrated Cu^{II} ions, existing mainly as square planar $[Cu(H_2O)_4]^{2+}$ and/or octahedral $[Cu(H_2O)_6]^{2+}$ species and in this case the dimeric unit in 2, also found to be the most stable conformation from the theoretical studies, is formed upon complexation with the ligand.

4. Conclusion

We presented herein an extension of our systematic study on pseudopeptidic ligands. In this work, we have shown that the self-assembly of isophthaloylbis- β -alanine and Cu^{II} ions is radically depended on the nature of the Cu^{II} starting material. Theoretical studies showed that compounds **1** and **2** are the thermodynamically most favourable products. Having gained this knowledge from this study and having in mind that structural motifs for such kinds of pseudopeptidic ligands can be readily reproducible [7a,d], we will focus our following efforts to synthesize porous CPs using such pseudopeptidic ligands and to characterize those compounds not only through single crystal X-ray, but also though powder diffraction studies using Rietveld refinements. Our major focus will be on optimising the production of highly porous compounds.

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Appendix A. Supplementary data

CCDC 977089 and 977090 contains the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10. 1016/j.poly.2015.01.023.

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