Four new complexes of chelidamic acid (H$_3$cda) in the presence of 2-aminopyrimidine (apym) or 2,4,6-triamino-1,3,5-triazine (tata) as external ligands, namely (apymH)[VO$_2$(H$_2$cda)]·H$_2$O (1), [Ni(H$_2$cda)(apym)(H$_2$O)$_2$]·H$_2$O (2), (apymH)[Fe(H$_2$cda)$_2$] (3), and (tataH)$_2$(tata)$_2$[Ca$_2$(H$_2$cda)$_2$(H$_2$O)$_6$]·H$_2$O (4) were synthesized. X-ray diffraction analysis of 1-4 revealed the formation of 3D frameworks generally involving weak interactions (mainly H-bonds) between metal complexes of chelidamic acid, protonated or deprotonated external ligands apym or tata and co-crystallized water molecules. Some complexes present remarkable assemblies in the solid state governed by unconventional non-covalent interactions that have been analyzed by means of DFT calculations. Solution studies were also performed to fully characterize the new compounds.

Introduction

In the design and synthesis of metal-organic framework (MOF) structures having potential applications as functional materials,[1] the bonding properties of the chosen ligands with binding sites in an appropriate spatial arrangement, and the steric-chemical preferences of the metal ions are the most important factors to consider for controlling the topology of the ensuing products via self-assembly.[2] Weak intra- and intermolecular interactions such as H-bonding and π–π stacking interactions can also be utilized in regulating the crystallization process.[3]

In this context, pyridinedicarboxylic acids have been widely used in recent years as organic multi-dentate building blocks for the construction of organic-inorganic hybrid materials, which are of great interest due to their potential applications in many areas, such as catalysis, antibacterial activity, enzyme inhibitors, aqueous solution chemistry, surface chemistry, magnetism and fluorescence.[4,5,6]

Interestingly, while coordination polymers prepared from pyridine-2,6-dicarboxylate or dipicolinate (dipic$^2-$, Scheme 1) are quite numerous,[6a,7,8,9,10] those obtained from 4-hydroxypyridine-2,6-dicarboxylate or chelidamate (Hcda$^2-$, Scheme 1) are less reported[11,12,13] despite this ligand is of great interest due to its usage in many areas of sciences, including biochemistry and medical chemistry.[14] Both ligands have a rigid 120° angle between the central pyridine ring and the two carboxylic(ate) groups, thus providing various coordination motifs under appropriate synthetic conditions for main group and transition metals, and actinides. Extended structures can be achieved by supramolecular π–π stacking interactions between adjacent coordinated dipic$^2-$/Hcda$^2-$ anions or by H-bonding between carboxylic oxygen acceptors and both solvent and external ligand donor O-H/N-H groups. In the case of Hcda$^2-$, the phenolic O-H group is also available for H-bond networking.

Therefore, in order to extend the investigation in this field and to obtain novel extended structures based on Hcda$^2-$, so to have a deeper knowledge on the coordination behavior of this ligand, we have reacted V$^{IV}$, Ni$^{II}$, Fe$^{III}$, and Ca$^{II}$ with H$_3$cda in water in the presence of 2-aminopyrimidine (apym) or 2,4,6-tri-
amino-1,3,5-triazine (tata) as external ligands. The isolated complexes (apymH)[VO\textsubscript{2}(H\textit{cda})]H\textsubscript{2}O (1), [Ni(H\textit{cda})(apym)(H\textsubscript{2}O)]\textsubscript{2}H\textsubscript{2}O (2), (apymH)[Fe(H\textit{cda})\textsubscript{2}] (3), and (tataH\textsubscript{2})(tata)[Ca\textsubscript{2}(cda)](H\textsubscript{2}O)\textsubscript{2}H\textsubscript{2}O (4) were characterized by X-ray diffraction analysis. Solution studies have also been performed to understand the behavior of the ternary systems M\textsuperscript{2+}/H\textit{cda}/apym (M\textsuperscript{2+} = VO\textsuperscript{2+}, Ni\textsuperscript{2+}, Fe\textsuperscript{2+} and Ca\textsuperscript{2+}/H\textsubscript{2}apym/tata.

Results and Discussion

3.1. Synthesis

Over the past decade, we have been interested in the syntheses, structural features and coordination behavior towards metal ions of proton-transfer compounds obtained by reacting organic donor ligands (D) containing N, S, and O heteroatoms and aromatic or aliphatic polycarboxylic acids, including H\textsubscript{2}dipic and H\textsubscript{2}cda (Scheme 1) (it is generally accepted that the reaction of an acid with a base will form a proton-transfer salt if the ΔpK\textalpha = pK\textalpha (base) - pK\textalpha (acid) is greater than 2 or 3). The versatility of proton-transfer compounds in the construction of organized inorganic supramolecular arrays resides in their ability to act as complexing agents towards metal ions in polar solvents such as water. Furthermore, in the resulting systems, counter ion species (DH\textsuperscript{+}) control the self-assembly of metal complex-organo-networks via simultaneous ionic and H-bonding interactions with the anionic metal complexes of the polycarboxylate ligands.

Starting, therefore, from the \textit{in situ} preformed proton-transfer compound (apymH\textsubscript{2} H\textsubscript{2}CDA) and the appropriate metal salts in 2:1 molar ratio, crystal corresponding to the formulation (H\textit{cda})\textsubscript{2}[Ca\textsubscript{2}(H\textit{cda})]H\textsubscript{2}O (1), [Ni(H\textit{cda})(apym)(H\textsubscript{2}O)]\textsubscript{2}H\textsubscript{2}O (2) and (apymH)[Fe(H\textit{cda})\textsubscript{2}] (3) were obtained from aqueous solutions after slow evaporation of the solvent. The complex (H\textit{tata})(tata)[Ca\textsubscript{2}(cda)](H\textsubscript{2}O)\textsubscript{2}H\textsubscript{2}O (4) was also obtained following a similar procedure but starting from the preformed proton-transfer compound (tataH\textsubscript{2})(H\textsubscript{2}CDA). An X-ray diffraction analysis of the four complexes was undertaken to understand their nature.

X-ray crystal structure of (apymH)[VO\textsubscript{2}(H\textit{cda})]H\textsubscript{2}O (1)

The molecular structure of 1 consists of one discrete mononuclear anionic complex [VO\textsubscript{2}(H\textit{cda})], shown in Figure 1, one (apym\textsuperscript{+})\textsuperscript{−} cation fragment and one uncoordinated water molecule.

The vanadium(V) atom exhibits an overall penta-coordination with a distorted trigonal-bipyramidal geometry where equatorial coordination comes from the pyridyl nitrogen atom (N1) and two oxo ligands (O7 and O6), while two carboxylate oxygen atoms (O1 and O4) from the tridentate H\textit{cda}− ligand occupy the axial positions (Figure 1). A similar coordination environment with the VO\textsubscript{2} group in a \textit{cis} configuration and the carboxylate oxygen atoms coordinated \textit{trans} to each other, has already been observed in the previously reported V\textsuperscript{V} complexes (NMe\textsubscript{2})[VO\textsubscript{2}(H\textit{cda})]H\textsubscript{2}O, K[VO\textsubscript{2}(H\textit{cda})]H\textsubscript{2}O and Na[VO\textsubscript{2}(H\textit{cda})]H\textsubscript{2}O (2).

X-ray crystal structure of [Ni(H\textit{cda})(apym)(H\textsubscript{2}O)\textsubscript{2}]H\textsubscript{2}O (2)

The structure of 2 consists of one neutral [Ni(H\textit{cda})(apym)(H\textsubscript{2}O)\textsubscript{2}] (Figure 4) complex unit and one water molecule in the asymmetric unit. The nickel(II) ion exhibits an overall hexacoordination with a distorted octahedral geometry where equatorial coordination comes from the pyridine N atom and one O atom from each of the two carboxylates of a coordinated H\textit{cda}− anion along with one pyrimidine N atom of apym located in \textit{trans}-position to the pyridine N atom of H\textit{cda}−. Two axial coordinate water molecules complete the coordination sphere. A similar coordination geometry for nickel(II) has been observed in the compound [Ni(H\textit{cda})(H\textit{cda})\textsubscript{2}]1.5H\textsubscript{2}O\textsuperscript{19} where three water molecules are directly coordinated to the metal center.
It is interesting to note that differently to what observed in complexes 1, 3, and 4, complex 2 features a neutral apym unit coordinated to the nickel ion. The resulting neutral complexes pack in order to maximize both p-p interactions involving the Hcda$^{2-}$ and apym rings, and H-bonds (Figures 5, Table S1) involving the free and coordinated water molecules, the phenoxy OH group, the coordinated carboxylic groups, and the uncoordinated N atom of the apym ligand. The assembly can be described as interacting [Ni(Hcda)(apym)(H$_2$O)$_2$] complex units forming corrugated sheets as that showed in Figure 5 and evidenced in monochromatic green in Figure 6. The sheets pack in the crystal lattice along the c direction (Figure 6).

X-ray crystal structure of (Hapym)[Fe(Hcda)$_2$] (3)

The molecular structure of 3 consists of one discrete mononuclear anionic complex [Fe(Hcda)$_2$]$^-$ and one (apym)$^+$ cation (Figure 7). The iron(III) ion is coordinated by two Hcda$^{2-}$ anions acting as tridentate ligands in a distorted octahedral coordination geometry. The two coordinated Hcda$^{2-}$ units lay on almost perpendicular planes with Fe–O bond distances in the range 1.9992(10)–2.0695(10) Å, and almost equivalent Fe–N lengths 2.0404(11), 2.0510(12) Å.

The packing of the complexes is governed by the numerous H-bonds engendered by the presence of several charged...
and neutral functional groups (carboxylate, pyridinium, hydroxy, and amino) able to interact among each other. In the solid state architecture of 3, the main motif can be recognized in ladders formed by symmetry related C1(7) chains, running along the a direction, made of [Fe(Hcda)(apym)]⁻ anionic units interacting through the strong O3A–H O3A···O4i and O3–H O3···O2 ii (a and b in Figure 8 and Table S1) H-bonds involving the OH groups and the coordinated carboxylates.

In Figure 9 shows how the ladders (orange colored) are held together by H-bonds (e–k Table S1 and Figure 9) involving both the amino and pyrimidinium N–H groups in the apym Hcations (blue colored) and the carboxylate units of coordinated Hcda⁻–ligands. The amino-pyrimidinium cations and the N1A–C5A rings of the relevant Hcda⁻ units are also involved in p···p interactions (apym)⁺···(Hcda)⁻···(Hcda)⁻···(apym)⁻ connecting four facing parallel or almost parallel units (p₁ and p₂, Figure 9).

Interestingly, 3 is isosctructural to reported complexes ([apy]⁻[Fe(dipic)₂] and [acr][Fe(cda)]⁻ (apy = 2-aminopyridine; acr = acridine).[18]

The structure of compound 4 consists of a discrete binuclear [Ca₂(cda)₂(H₂O)₆]⁺ complex anion, sitting on an inversion centre, in which each metal centre adopts a heptacoordinated pentagonal bipyramidal geometry (Figure 10). Two (tataH)⁻ counter cations, two uncoordinated tata units and a water molecule complete the asymmetric unit.

The calcium ions are coordinated by a water molecule and two cda⁻ ligands in the equatorial plane, and two coordinated water molecules in the axial positions. The cda⁻ units behave as tridentate "m²-h₂,h₁,h₁" ligands, with the heterocyclic N1 and the O4 oxygen atoms bound to metal ions and the O1 oxygen...
atoms bridging the calcium ions [Ca–O1 2.3956 (19), Ca1–O1 ’ 2.4792 (18)] (Figure 10). The phenolic O-H groups are deprotonated, an unusual feature for metal complexes of chelidamic acid, which has been already observed in two of the four cda units of the complex (H2daprop)2 [Ca2(Hcda)2(H2O)2]2– (daprop = 1,3-diaminopropane). In this case the two metal centers are bridged via four chelidamic units: two feature a protonated O-H function and bind the two metal centers as in 4, the other two take the place of the four axial water molecules in 4 and bridge the two metal centers through the carboxylate groups with an internal proton transfer from the phenolic functions to the pyridine nitrogen atoms, which therefore, are not coordinated to the metal.[19]

[Ca2(cda),(H2O)]2– units interact each other via Ow–Hw···O H-bonds involving the coordinated water molecules (see Table S1, Figure S3) and the phenolate oxygen atoms to give 2D assemblies in the (110) plane (Figure 11).

Triaminotriazine units interact via N–H···N H-bonds to form ribbons along the [110] direction which stack along the [1-10] direction (Figure 12).

The crystal packing of 4 is built by an alternate disposition along c of sheets of [Ca2(cda),(H2O)]2– anionic units (yellow colored in Figure S3) and stacks of triaminotriazine units (yellow colored in Figure S3) held together via H-bonds mainly involving the uncoordinated water molecules (red colored in Figure S3).

Theoretical study

We have analyzed the noncovalent interactions observed in the solid state of compounds 1–4 energetically focusing our attention to the anion–π, π–hole and antiparallel π–π interactions. Particularly π–hole interactions are increasing attention in supramolecular chemistry and crystal engineering fields.[20]

In the crystal structure of compound 1 we have observed an interesting assembly (see Figure 13A) where the anionic [VO2(Hcda)]2– complex and the aminopyrimidinium cation (apymH) ion-pair are antiparallel stacked to other ion pairs forming infinite columns. Interestingly, the Hcda ligand is stacked to the H-bonding array resembling a salt-bridge–π interaction. We have computed the Molecular Electrostatic Potential Surface (MEPS) of (apymH)[VO2(Hcda)]2– ion-pair to investigate the positive and negative regions and rationalize the interactions (see Figure 13B xfigr13 >). The most positive region corresponds to the N–H that establishes an H-bond with the lattice water molecules. It can be observed a positive re-
Figure 10. View of [(tata)₂(C₅H₆O₆)₂H₂O]⁻ (4) with the atom numbering scheme adopted, displacement ellipsoids are drawn at 50% probability level. Selected bond distances and angles: Ca1–O1 2.3956(l9); Ca1–O1W 2.354(2); Ca1–O2W 2.364(2); Ca1–O4 2.3998(18); Ca1–O3W 2.417(2); Ca1–N1 2.428(2); Ca1–O1 2.4792(18); Ca1–Ca1i 3.9244(10). Symmetry code: i 2–x, 1–y, 1–z.

Figure 11. View along c of 2D assembly of [(C₅H₆O₆)₂(H₂O)₂]⁻ anionic units in 4 interacting via Ow–Hw···OH₂+ H-bonds. a: O1w–H1wA···O3 ii 1.75; 2.653(3); 170; b: O1w–H1wB···O5 iii 1.85; 2.637(3); 159; c: O2w–H2wB···O3 1.90 Å; 2.683(3) Å; 176°. Symmetry codes: a: 1–x, 1–y, 1–z; b: 1+x, 1+y, z; c: 1+x, y, z.

Figure 12. View along c of H-bonded ribbons of triaminotriazine units in 4 stacked along the [0-10] direction. d: N5–H5B···N8 2.24; 3.063; 171°; e: N7–H7B···N10 2.18; 3.005(3); 177°; f: N11–H11B···N2’ 2.24 Å; 2.999(3) Å; 172°; g: N13–H13B···N4’ 2.15 Å; 2.980(3) Å; 178°. Symmetry codes: a: 2–x, 1–y, 2–z; b: 1–x, –y, 2–z.

Critical points (CP) and bond paths of the dimer is shown in Figure 13D. This distribution shows that the dimer presents two hydrogen bonds between the VO₂⁺ moiety and one H atom of the apymH ring. Each H-bond is characterized by a bond CP (red sphere) that connects the O atom to the H atom. Moreover, two symmetrically equivalent anion–π interactions are also established between the coordinated carboxylate group and the apymH π-system. Each interaction is characterized by the presence of three CPs that connect the three atoms of the R–COO⁻ group to three atoms of the apymH ring. The presence of this interaction agrees well with the MEP analysis, since the MEP value over the apymH is large and positive in the region of the carboxylate (see Figure 13B). Finally, the π–π interaction is characterized by the presence of three bond CPs that connect both Hcda rings. The arrangement of the rings in the π–π interaction also agrees well with the MEP analysis commented above, since the MEP over this ring is small, thus reducing the electrostatic repulsion and consequently, other contributions like dispersion and polarization terms can dominate the π–π interaction.

In the crystal structure of compound 2 we have observed the formation of an infinite ladder (see Figure 14A) as a consequence of the electrostatically favored stacking interactions between the [Ni(Hcda)(apym)H₂O]₃ complexes with H-bonds established between the coordinated water molecules as acceptors (C–H···OH₃) and donors (HOH···O). The π-interaction is established between the Hcda and apym rings. We have rationalized this fact by computing the MEP surface (see Figure 14B). The most positive region corresponds to the H atoms of the coordinated water molecules. It can be also observed that the MEP over the π-system of the apym ring is pos-
itive due to the coordination to the metal center that enhances the \(\pi\)- acidity of the ring. Moreover, the electrostatic potential over the \(\pi\)-system of Hcda ring is small but negative. Therefore the stacking observed in the solid state is electrostatically favored. We have computed the interaction energy of one dimer extracted from this infinite ladder (\(\Delta E_2 = -15.3\ \text{kcal/mol}\), see Figure 14C), which is large and negative due to the combination of \(\pi-\pi\) and HB interactions. The HB-bonding interaction between the water molecule and the OH phenolic group is very short (1.86 Å) due to the enhanced acidity of the H atoms of the coordinated water molecule (see MEP value in Figure 14B).

In an effort to evaluate the contribution of this H-bond, we have computed an additional model (see Figure 14D) where the OH group has been replaced by an H atom, and consequently this H-bond is not established. As a consequence the interaction energy is reduced to \(\Delta E_3 = -9.0\ \text{kcal/mol}\). The AIM distribution of CPs is shown in Figure 13E. Each H-bond is characterized by a bond CP (red sphere) that connects the O atom to the H atom. Moreover, the \(\pi-\pi\) interaction is characterized by the presence of two bond CPs that connects both aromatic rings. This interaction is further characterized by the presence of a ring CP (yellow sphere) due to the formation of a supramolecular ring.

In the crystal structure of compound 3 we have observed the formation of an infinite column (see Figure 15A) as a consequence of the interaction of the \((\text{apymH})\left[\text{Fe(Hcda)}_2\right]\) ion-pair with the adjacent ion pair by means of two H-bonds and a \(\pi\)-hole interaction. Interestingly, the \(\pi\)-hole interaction is established between the O atom of the carboxylate group of one ion-pair and the C atom of the coordinated carboxylate group of the other ion-pair. The O⋯C distance (2.88 Å) is considerably shorter than the sum of van der Walls radii (3.22 Å). We have computed the interaction energy of a dimer extracted from the infinite column (Figure 15B), which is very favorable (\(\Delta E_4 = -32.0\ \text{kcal/mol}\)) due to the combination of \(\pi\)-hole and two HB interactions. We have also computed another theoretical model where we have modified the aromatic ring of one Hcda ligand (see Figure 15C), and consequently both H-bonds are not established. As a consequence the interaction energy is reduced to \(\Delta E'_4 = -17.3\ \text{kcal/mol}\). This interaction energy is too large compared to the reported \(\pi\)-hole interactions. To further investigate this issue, we have characterized the dimer using the Bader’s theory of “atoms in molecules” (AIM), see Figure 14D. The distribution of CPs demonstrates the existence of the H-bond and \(\pi\)-hole interactions described above (each one characterized by a bond CP). Moreover, the AIM also reveals the presence of an additional H-bond between an H-atom of the cationic apymH ring and an O-atom of the anionic complex. This interaction further contributes to the stabilization of the assembly and explains the large \(\Delta E'_4\) interaction energy.

Finally, in complex 4, we have analyzed the H-bonding network that is responsible of the formation of the interesting assembly in the solid state, represented in Figure 16A. The anionic dinuclear complex \([\text{Ca}_2(\text{Hcda})_2(\text{H}_2\text{O})_6]^{2-}\) and the counterions \((\text{Htata})^+\) interact with neutral tata molecules by the simultaneous formation of four H-bonds. We have evaluated the interaction energy of this assembly that is \(\Delta E_5 = -20.1\ \text{kcal/mol}\) using the reaction shown in Figure 16B. Therefore the interaction corresponds to the contribution of the four H-bonds. Interestingly, the protonated ligands \((\text{Htata})^+\), which also form H bonding interactions with the dianionic complex, participate in \(\pi\)-hole bonding interactions (represented by red dashed lines in Figure 16). The lone pair of the amino group is located exactly over the C atom of the \(\text{Ca}^2+\)-coordinated carboxylate group at 2.99 Å (less than the sum of van der Waals radii). The AIM dis-

---

**Figure 13.** A) X-ray fragment of compound 1. B) MEP surface of the ion pair. C) Theoretical model used to evaluate the noncovalent interactions. D) AIM distribution of bond (red spheres), ring (yellow spheres) and cage (green spheres) critical points. The bond paths are also represented.
distribution of CPs confirms the existence of this interaction since one bond CP connects the N atom to the C atom of the CO$_2$–Ca group (see Figure 16C)

Solution studies

In order to evaluate the stoichiometry and stability of the ternary Fe$^{3+}$ and Ni$^{2+}$ complexes with apym/H$_3$cda and the ternary Ca$^{2+}$ complex with tata/H$_3$cda in aqueous solution, known

Figure 14. A) X-ray fragment of compound 2. B) MEP surface of the ion pair. C and D) Theoretical models used to evaluate the noncovalent interactions. E) AIM distribution of bond (red spheres) and ring (yellow spheres) critical points. The bond paths are also represented.

Figure 15. A) X-ray fragment of compound 3. B and C) Theoretical model used to evaluate the noncovalent interactions. (D) AIM distribution of bond (red spheres) and ring (yellow spheres) critical points. The bond paths are also represented.
concentrations of fully protonated ligands and their 1:1 mixtures in the absence and presence of the metal ions were titrated with a 0.099 M solution of NaOH at 25 °C, while an ionic strength of 0.1 M was maintained by NaClO4. Titration continued before precipitation. Similar studies were performed for VO2+/ (using VCl3 as starting salt) but hydrolysis of the oxocation in the experimental conditions used prevented the investigation. It was found that H3cda has good interaction with metal ions, because the potentiometric titration curves were depressed considerably in the presence of the metal ions (see SI, Figures S4-S6).

The extent of depression obviously depends both on the stoichiometry of resulting complexes and the ability of the metal ion to bind the ligand components. The cumulative stability constants, $\beta_{\text{global}}$, are defined by Eq. (1) (charges are omitted for simplicity)

$$\text{mL} + \text{lL} + q\text{Q} + h\text{H} \leftrightarrow M_m\text{L}_l\text{Q}_q\text{H}_h \beta_{\text{global}}$$

Where M is Ni2+, Ca2+ or Fe3+ ions, L is Hcda2−, Q is apym or tata and H is proton, and m, l, q, and h are the respective stoichiometric coefficients. Since the ligand and complex activity coefficients are unknown, the $\beta_{\text{global}}$ values are defined in terms of concentrations. The errors are minimized by using a high-constant ionic strength of 0.1 M and low ligand concentrations (in the order of $10^{-3}$ M).

The potentiometric pH titration profiles of H3cda, apym and their 1:1 mixture in the presence of Ni2+ (1 equiv) and Fe3+ (0.5 equiv) ions, and H3cda, tata and their 1:1 mixture in the presence of Ca2+ ions (1 equiv), were fitted with the program BEST[27] and the calculated stability constants for the most likely complexed species in aqueous solution are reported as supplementary materials.

Evaluating acidity constants of chelidamic acid at 25 °C with BEST program (10.89, 2.9 and 2.01) agrees with results reported in the literature (see Table S2, SI).[21,22] In the case of Ni2+, calculated stability constants, log $\beta$ of 1:1 and 1:2 complexes with Hcda2− were 8.62 and 16.44 respectively, agrees with values previously reported, 9.2 and 17.3.[23] Sample species distribution diagram for L/Q mixtures in presence of Ni2+, Ca2+ and Fe3+ are shown in Figure 17.

The percent is based on abundance of species relative to abundance of (Hcda)2− (L). It is obvious from Figure 17 and Tables S3-S5 in the SI that in all three cases, among the evaluated species in solution there are also those corresponding to the complexes isolated in the solid state.

These titration studies are in good agreement with previous results available in the literature for [acrH][Fe(cda)]18b and [9a-acrH]2[Ni(cda)], (9a-acr = 9-amineacridine).[24]

Conclusions

In conclusion, a series of complexes with chelidamic acid, the mononuclear (apymH)[VO2(Hcda)]·H2O (1), [Ni(Hcda)(apym)H2...
molecules completing the coordination sphere. The different stoichiometries and charges of the obtained metal complexes balanced by (apymH)\(^{+}\) (1, 3) or (tataH)\(^{-}\) (4) cations are reflected in different crystal packings and structural architectures observed in the solid state which are determined mainly by H-bonding interactions between anions and cations but also H-bonding interactions involving uncoordinated water molecules and in the case of 4, neutral tata units. These results confirm the versatility of chelidamic acid together with the most known dipicolinic acid as multi-dentate building blocks for the construction of organic-inorganic hybrid materials. Finally, the influence of unconventional noncovalent interactions (π-hole) have been analyzed energetically using DFT calculations and confirmed using the Bader’s theory of AIM.

Acknowledgements

The authors thank to the Ferdowsi University of Mashhad and The Fondazione Banco di Sardegna for financial support of this work (Grant No. P/2106). A.B. and A.F. thank DICYT of Spain (projects CTQ2014-57393-C2-1-P and CONSOLIDER INGENIO CSD2010–00065, FEDER funds) for funding. We thank the CTI (UBI) for free allocation of computer time.

Keywords: MOFs · X-ray structures · Crystal structure · Solution studies · DFT calculations
