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Neutral and Cationic Chelidonate Coordination Polymers with *N,N'*-Bridging Ligands

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Abstract: The biomolecule chelidonic acid (H2chel, 4-oxo-4*H*-pyran-2,6-dicarboxylic acid) has been used to build new coordination polymers with the bridging *N*,*N'*-ligands 4,4'-bipyridine (4,4-bipy) and 1,2-bis(4-pyridyl)ethane (bpe). Four compounds have been obtained as single crystals: 1D cationic coordination polymers $[M(4,4-bipy)(OH_2)_4]^{2+}$ with chelidonate anions and water molecules in the second coordination sphere in $1_{\infty}[Zn(4,4-bipy)(H_2O)_4]$ chel·3H₂O (**2**) and in the two pseudopolymorphic $1_{\infty}[Cu(4,4-bipy)(H_2O)_4]$ chel·nH₂O (*n* = 3, **4a**; *n* = 6, **4b**), and the 2D neutral coordination polymers $2_{\infty}[Zn(chel)(4,4-bipy)(H_2O)]\cdot2H_2O$ (**1**) and $2_{\infty}[Zn(chel)(bpe)(H_2O)]\cdotH_2O$ (**3**) where the chelidonate anion acts as a bridging ligand. The effects of the hydrogen bonds on the crystal packing were analyzed. The role of the water molecules hosted within the crystals lattices was also studied.

Keywords: zinc complexes; copper(II) complexes; coordination polymers; chelidonic acid; metallosupramolecular compounds; H-bonding pattern; X-ray diffraction

1. Introduction

Chelidonic acid (H2chel, 4-oxo-4H-pyran-2,6-dicarboxylic acid) is a biomolecule found in several plants and is considered to be an active component of some medicinal herbs [1]. The compound exhibits some pharmacological effects such as mild analgesic, antimicrobial, oncostatic and sedative [2] effects and its therapeutic potential in allergic disorders [1], intestinal inflammation [2] and regulation of depression associated with inflammation [3] have been investigated. From the point of view of coordination chemistry, H2chel after deprotonation is an angular dicarboxylate that can act as a linker between metal ions to yield coordination polymers. From the supramolecular point of view, chel²⁻ presents several oxygen atoms that can act as hydrogen acceptors towards biologically important hydrogen donors such as water molecules. In this way, the dianion chelidonate can be considered a biologically and environmentally interesting building block for the construction of new metallosupramolecular compounds. This kind of building blocks offers advantages such as its natural availability, the presence of various metal-binding sites which allow the display of different coordination modes and consequently a structural diversity and the possibility of establishing different hydrogen bonds patterns in aqueous media.

Several structural studies on metal chelidonates that are coordination polymers of different dimensionality can be found in the literature: 1D compounds with Zn(II) [4], Cu(II) [5,6], Dy(III)-Ba(II) [7] or Lu(III) [8], 2D systems with several lanthanide cations [8] and also with Cu(II) [9] and 3D polymers with Cd(II) [5], Cu(II) and Ag(I) [9], Pr(III),

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses /by/4.0/). Nd(III), Sm(III), Lu-Ba and Sm-Ba [7] and with Ba(II) [10]. In all these compounds the chelidonate is the only ligand used. However, the structural information available on mixed ligand chelidonate coordination polymers is scarce. To the best of our knowledge only a few examples have been reported: 1D coordination polymers with monodentate ligands such as pyridine [11] or dmso [12] and with the bidentate chelating ligand 2,2′-bipyridine [13], which also stabilised the 2D copper(II) coordination polymer ²_∞[Cu(chel)(bipy)] [13]. In all of these coordination polymers the chelidonate dianion behaves as a bridging ligand between two, three or four metal centres with the coordination modes shown in Scheme 1.



Scheme 1. Coordination modes of the chelidonate ligand in coordination polymers.

In view of these previous results on the role of the chelidonate anion in coordination polymers, we decided to study its coordinative possibilities and supramolecular role in aqueous media in systems that contain the bridging N_rN' -ligands $4_rA'$ -bipyridine (4_rA -bipy) and 1_rA -bis(4-pyridyl)ethane (bpe), which can facilitate the extension of the metalligand interaction in at least one direction. The aim of this work was to prepare crystalline solids of coordination polymers formed with chelidonate anions to analyse their coordinative behaviour, searching for new coordination modes, and to study their participation in the supramolecular arrangements, searching for new hydrogen bond patterns in aqueous media.

We report here the diffusion solvent crystallization, structural characterisation and supramolecular structures of the 2D neutral coordination polymers ${}^{2}_{\infty}$ [Zn(chel)(4,4-bipy)(H₂O)]·2H₂O (**1**) and ${}^{2}_{\infty}$ [Zn(chel)(bpe)(H₂O)]·H₂O (**3**), in which the chelidonate anion acts as a bridging ligand. The cationic 1D coordination polymer ${}^{1}_{\infty}$ [Zn(4,4-bipy)(H₂O)₄]chel·3H₂O (**2**) and its analogues ${}^{1}_{\infty}$ [Cu(4,4-bipy)(H₂O)₄]chel·nH₂O (*n* = 3, 4a; *n* = 6, 4b), with the chelidonate anion in the second coordination sphere, were also obtained and structurally characterised.

2. Results and Discussion

2.1. Preparation and Spectroscopic Characterisation of Complexes

The synthetic procedure for the preparation of the target compounds is shown in Scheme 2. The slow diffusion at room temperature of aqueous solutions of the 1D coordination polymer ${}_{-\infty}[Zn(chel)(H_2O)_2]$ [4] and ethanolic solutions of the two *N*,*N'* bridging ligands 4,4'-bipyridine (4,4-bipy) and 1,2-bis(4-pyridyl)ethane (bpe) led to the formation of single crystals of the neutral 2D coordination polymers ${}_{-\infty}^2[Zn(chel)(4,4-bipy)(H_2O)]\cdot 2H_2O$ (1) and ${}_{-\infty}^2[Zn(chel)(bpe)(H_2O)]\cdot H_2O$ (3). After the separation of crystals of 1 the remaining solution was left to evaporate at room temperature and single crystals of the 1D cationic coordination polymer ${}_{-\infty}^1[Zn(4,4-bipy)(H_2O)_4]$ chel·3H₂O (2), with the

uncoordinated chelidonate anion, were isolated. Polymer 2 contains the 1_{∞} [Zn(4,4bipy)(H2O)4]²⁺ cation, which was also found in several crystalline compounds with other anions such as nitrate [14], biphenyldisulfonate [15], sulfobenzoate [16], sulfamoylbenzoate [17], succinate [18], barbiturate [19] and perchlorate [20] in the second coordination sphere. After a CSD search [21] it was verified that the formation of the polymeric species $l_{\infty}[M(4,4-bipy)(H_2O)_4]^{2+}$ is observed for other metal centres in the presence of different anions in the outer coordination sphere. Some examples are Mn(II) or Co(II) with 4-aminobenzenesulfonate [22], Fe(II) or Co(II) with croconate [23], Co(II) (furandicarboxylate, with several polycarboxylates benzenetricarboxylate, benzenetetracarboxylate [24] and 3,3',4,4'-biphenyltetracarboxylate [25]), Ni(II) with 1,2,4,5-benzenetetracarboxylate, Ni(II) or Cu(II) with 2,6-naphthalenedisulfonate [26], Co(II), Ni(II) or Cu(II) with barbiturate [27] and Cd(II) with 1,3-propanedisulfonate [28].



Scheme 2. Synthetic procedure for the preparation of the compounds.

The frequent formation of such polymeric cationic species with different anions that can be considered as weakly coordinating suggests a remarkable stability for this cation. It was decided to explore whether it was possible to obtain the ${}^{1}_{\infty}$ [Cu(4,4-bipy)(H₂O)₄]²⁺ species with the uncoordinated chelidonate anion. After unsuccessfully attempting diffusion methods we carried out a reaction under reflux in H₂O/MeOH of a mixture of Cu(NO₃)₂/4,4-bipy and H₂chel/KOH. This led to the isolation of single crystals of the pseudopolymorphs ${}^{1}_{\infty}$ [Cu(4,4-bipy)(H₂O)₄]chel·nH₂O (n = 3, 4a; n = 6, 4b).

The IR spectra of all of the compounds exhibit broad bands of medium intensity at around 3400 cm⁻¹ corresponding to the OH stretching vibrations of the coordinated and crystallisation water molecules. The strong IR bands between 1600 and 1640 cm⁻¹ can be assigned to the $v_{asym}(OCO)$ vibration mode and the medium intensity bands at around 1360 cm⁻¹ are attributable to the $v_{sym}(OCO)$ vibration mode.

2.2. Structural Studies

All of the compounds described here were isolated as single crystals and their structures were elucidated by X-ray diffraction. The significant structural parameters for compounds **1–4** are listed in Tables S1 and S2, and crystal structure and refinement data are listed in Table S5.

Structural analysis revealed that all of the compounds are hydrates and that **2**, **4a** and **4b** are formed by cationic chains that are stabilised by chelidonate anions and water molecules. When the chelidonate ligand is coordinated to the metal centre and forms part of the structural backbone, the resulting compounds are 2D coordination polymers, as revealed by X-ray analysis of **1** and **3**.

2.3. Crystal Structures of the Cationic Polymers 2, 4a and 4b

The coordination environment of the metal ions and the 1D polymeric nature of compounds **2**, **4a** and **4b** are represented in Figure 1. A summary of the bond lengths and angles in the first coordination sphere is provided in Table 1.

The three structures are polymeric chains based on the cationic complexes $[M(4,4-bipy)(OH_2)_4]^{2+}$ (M = Cu(II) and Zn(II)), where the N-donor ligands act as a bridge between the metal centres. The second coordination spheres are formed by dianionic chelidonate anions and three or six water molecules. Complexes **4a** and **4b** crystallise in the orthorhombic chiral *P*2₁2₁2 and triclinic *P-1* space groups, respectively, and they can be considered pseudopolymorphs [29] since they have the same crystalline form, albeit with different numbers of water molecules trapped within the crystal networks.



Figure 1. Cationic chains in coordination polymers **2**, **4a** and **4b** showing in detail the coordination environment and the disposition of the 4,4-bipy rings.

All M^{II} metal centres are {N₂O₄}-hexacoordinated through the nitrogen bipy atoms in trans positions and four oxygen atoms belonging to four water molecules in the equatorial plane. The copper atoms in **4a** and **4b** are in an elongated octahedral environment and they exhibit the expected Jahn–Teller distortion, with four short metal–ligand bonds (Cu– O_{water} and Cu–N with distances of around 2 Å) and two longer bonds with water molecules (2.417(2) Å in **4a**, 2.291(2) and 2.173(3) Å in **4b**). Clearly the Jahn–Teller distortion is more pronounced in compound **4a**, where the pyridine rings of the 4,4'-bipyridine ligand are further from coplanarity, as shown in Figure 1.

In compound **2** the Zn–O and Zn–N distances are in the range 2.08–2.19 Å (Table 1) and the values for the orthogonal angles in the octahedral polyhedron are between 87.15 and 93.49°. Comparison of the orthogonality of the coordination octahedra in the three compounds shows that the smallest deviation is observed in the copper(II) compound **4b**, with values between 88.26 and 91.70°.

The intermetallic distance through the 4,4-bipy bridging ligand is shorter in copper polymers (11.176 Å in **4a** and 11.290 Å in **4b**) than in **2** (11.487 Å). The aromatic rings in 4,4-bipy are not coplanar and the angles between the planes are 23.02° and 13.72° in **4a** and **4b**, respectively, and the disposition is closer to coplanarity in **2** (around 6°) (Figure 1).

In all structures the second coordination sphere plays a crucial role in the supramolecular organisation. The cationic chains are connected by hydrogen bonds to the chelidonate anions and different numbers of water molecules to form different arrangements in each structure. The main hydrogen-bonding interactions responsible for the 3D crystal packing of compounds **2**, **4a** and **4b** are listed in Table S3. In all cases, the resulting supramolecular networks are formed and propagated through Ochelidonate...Owater

hydrogen bonds, with the formation of different association patterns such as rings, discrete associations or infinite layers.

In compound **2** the three uncoordinated water molecules are not associated with each other, so the notation W_1 has been selected to describe their isolated participation in the supramolecular organisation. One of the water molecules, O2w, and two chelidonate anions form a discrete dimer through H-bonding interactions to yield a four-membered ring, with O···O distances of 2.781 and 2.932 Å (Figure 2, Table S3). Another crystallisation water molecule, O1w, establishes H-bonding interactions with the two carboxylate groups of a chelidonate to form an eight-membered ring and the third water molecule is H-bonded with the ketonic oxygen of the chelidonate. In this way, all of the oxygen atoms of the chelidonate are involved as acceptors in hydrogen-bonding interactions.



Figure 2. Supramolecular arrangement of **2** showing in detail the interactions established between the crystallisation water molecules and chelidonate anions.

The cationic chains of **2** are anchored to these water-chelidonate dimers through Ow_{coord}...O_{carboxy} and Ow_{coord}...Ow_{crystallisation} interactions (Table S3). Cationic chains and the anionic units are arranged in an alternating manner to form the final supramolecular organisation (Figure 2).

In the structures of **4a** and **4b** chelidonate anions and water molecules are associated through different H-bonding interactions to form different anionic arrangements (Figures 3 and 4) that are extended in two dimensions, thus leading to anionic $[(H_2O)_nchel]^{2-}$ sheets. In this way, the layers act as the 'glue' between the cationic units to form the final metallosupramolecular arrangements [30]. This kind of 2D anion-water association has been observed in other cases, such as $[Ni(4,4-bipy)(H_2O)_4]\cdot 0.5(btc)\cdot H_2O$ (H₄btc, 1,2,4,5-benzenetetracarboxylic acid) [25]

In **4a** the crystallisation water molecules are also not interconnected by hydrogen bonds (W1 motif) and only one of them (O2w) is involved in the formation of the supramolecular [(H₂O)₃chel)]²⁻ layer (Figure 3), with O···O distances of 2.781(2) and 2.913(3) Å. These layers are parallel to one another and this arrangement produces columnar voids in which the cationic chains are placed and stabilised by several hydrogen bonds involving as donors the crystallisation and coordinated water molecules and as acceptors all of the oxygen atoms of chelidonate (Table S3).



Figure 3. Supramolecular arrangement of **4a** showing in detail the layers formed by the interaction of crystallisation water molecules and chelidonate anions.

In **4b** the six water molecules of crystallisation have three different arrangements, namely one isolated molecule (W1), a dimer (W2) and a trimer (W3) (Figure 4). The isolated molecule, O13w, corresponds to the W1 motif that is also present in all three compounds (2, 4a and 4b) with the same structural behaviour; as a donor this water molecule is connected with a chelidonate molecule by hydrogen bonds with two oxygen atoms from the two carboxylate groups (O···O distances of 2.721(3) and 2.723(3) Å in 4b) and as an acceptor with one or two coordinated water molecules of the corresponding cations. The other five water molecules are associated in a dimer (W2) with an O…O distance of 2.855(4) Å and in a trimer (W3) with shorter O···O distances (2.729(5) and 2.737(6) Å). The hydrogen-bonding interactions of these water molecule motifs with the chelidonate anions (Table S3) lead to the organisation of the second coordination sphere being anionic [(H₂O)₆chel]²⁻ ladder-shaped layers (Figure 4) that leave space to accommodate anchored through Owcoord...Ocarboxy the cationic units and Owcoord...Owcrystallisation interactions.



Figure 4. Supramolecular arrangement of **4b** showing in detail the layer formed by the interaction of crystallisation water molecules and chelidonate anions.

In the coordination polymers **2**, **4a** and **4b** the different collections of hydrogen bonds modulate the association of the chains and result in a similar packing degree, as indicated by the Kitaigorodskii indexes [31]; 70.1% in **4a**, 70.6% in **4b** and 72.1% in **2**.

	2	4a	4b
M-OH ₂	2.088(2)-2.105(2)	1.952(2)-2.417(2)	2.028(2)-2.291(2)
M–N	2.174(2)	2.049(3)	2.093(3)
	2.195(2)	2.031(3)	
cis angles	87.15(9)-93.49(9)	87.30(7)-92.70(7)	88.26(9)-91.70(9)
trans angles	174.83(10)-178.58(8)	174.59(15)-180.0	177.21(9)-179.90(10)

Table 1. Summary of bond lengths/Å and angles/° in the first coordination sphere of 2, 4a and 4b.

2.4. Crystal Structures of Neutral Polymers 1 and 3

The Zn(II) polymeric compounds **1** and **3** crystallise in the P-1 and P2₁/c space groups, respectively. The significant structural parameters are listed in Table S2 and a summary of bond lengths/Å and angles/° in the first coordination sphere is provided in Table 2. In both compounds, the two carboxylate groups of the chelidonate ligand are coordinated to the metal centre to produce monodimensional chains. These chains are bridged by the rigid 4,4-bipyridine or the more flexible 1,2-bis(4-pyridyl)ethane *N*-donor ligands to yield the final 2D coordination compounds (Figures 5 and 6).

Chelidonate acts in both structures as a bridging ligand in a μ -1 κ ²O^{III},O^{IV}:2 κ O^V coordination mode (Scheme 3), which has not been previously observed in other coordination polymers with this ligand. Each *N*-donor ligand acts as a bis-monodentate system to bridge zinc atoms with Zn···Zn distances of 11.346 Å and 13.434 Å in **1** and **3**, respectively. Chelidonate ligands also connect two zinc metal centres to produce similar Zn···Zn distances of 9.928 Å in **1** and 9.611 Å in **3**. In this way rhomboidal grid layer structures are formed.



Scheme 3. New coordination mode, μ -1 κ^2 O^{III},O^{IV}:2 κ O^V, of chelidonate in coordination polymers 1 and 3.

Each metal centre is in a distorted octahedral geometry, with two nitrogen atoms from N-donor molecules in a trans disposition in **1** and a cis arrangement in **3** (Zn–N distances are in the range 2.084–2.157 Å), three oxygen atoms from carboxylate groups of a chelidonate ligand and one oxygen atom from a water molecule (Zn–Ow distances are 2.032(3) Å in **1** and 2.158(2) Å in **3**). One carboxylate group of the chelidonate ligand is anisobidentate, with a bite angle of about 55°, one zinc metal has a short Zn–O distance (2.130(3) Å in **1** and 2.085(2) Å in **3**), the other has a longer distance of around 2.5 Å and the other carboxylate group is monodentate.



Figure 5. View of the 2D layers of ²_∞[Zn(chel)(4,4-bipy)(H₂O)]·2H₂O (**1**) and the final 3D supramolecular arrangement, showing the zinc atom environment and the corresponding labelling scheme.

Zinc-chelidonate chains and the bis-monodentate rigid 4,4-bipy bridging ligand form a rhomboidal grid layer in **1** within an sql topology, with rhomboid window dimensions of 11.35×9.93 Å and angles of 97° and 82° (defined by Zn…Zn distances and Zn…Zn…Zn angles). Further expansion of the length of the bidentate bipyridine ligand to bpe leads to the formation of a corrugated layer structure in **3** with rhomboidal void dimensions of 13.43×9.61 Å and angles of 97° and 82°.

	1	3
Zn-O(1W)	2.032(3)	2.158(2)
	2.015(3)	1.978(2)
Zn-Ochel	2.539(3)	2.557(2)
	2.130(3)	2.085(2)
Ze N	2.151(4)	2.147(2)
ZII-IN	2.157(3)	2.084(2)
cis angles	82.27(12)-116.83(12)°	88.37(8)-97.42(8)
trans angles	149.06(11)-169.87(14)°	138.00(8)–169.69(9)°

Table 2. Summary of bond lengths/Å and angles/° in the first coordination sphere of [Zn(chel)(4,4-bipy)(H2O)]·2H2O (1) and [Zn(chel)(bpe)(H2O)]·H2O (3).



Figure 6. Structure of [Zn(chel)(bpe)(H₂O)]·H₂O (**3**) showing the zinc atom environment and the corrugated disposition of the layers.

The aromatic rings in 4,4-bipy are not coplanar and show a deviation of 42° in 1, which is clearly higher than the values observed in the polymeric chains of 4a and 4b. The bpe linkers in 3 are twisted with respect to each other through an anticlinal torsion angle of 167.4° (through C–CH₂–CH₂–C) indicating an anti conformation.

The layers in **1** are stacked along the *b* axis to yield a final 3D arrangement with an ABAB stacking mode (Figure 5). These layers are connected by means of hydrogen bonds involving the coordinated water molecule and oxygen atoms from carboxylate groups of neighbouring layers (d(O1W...Ochel) = 2.699(4) and 2.772(5) Å; Table S4, detail shown in Figure 5). The two-crystallisation independent free water molecules (W1) are located in the voids of the rhomboidal grids (Figure 5) and are weakly attached to the 2D layers.

The supramolecular arrangement in the corrugated layers of **3** is achieved by means of the same supramolecular synthon described above for compound **1**: hydrogen bonds involving the coordinated water molecule and oxygen atoms from carboxylate groups of neighbouring layers (d(O1W...Ochel) = 2.762(3) and 2.825(3) Å, Table S4 and detail in Figure 7). As in compound **1**, the only crystallisation water molecule (W1) is weakly attached to the metal organic framework through a hydrogen-bonding interaction with the ketonic group of a chelidonate ligand (d(Ow...O) = 3.125(5) Å).

In both structures the layers are packed efficiently, as evidenced by the Kitaigorodskii [31] packing indexes of 64.9% in **1** and 69.7% in **3**.



Figure 7. View of the 3D supramolecular arrangement in [Zn(chel)(bpe)(H₂O)]·H₂O (**3**) showing details of the of O1w–H1w…O hydrogen-bonding interactions.

3. Experimental

3.1. Materials and Physical Measurements

All reagents and solvents were obtained commercially and were used as supplied. Elemental analysis (C, H, N) was carried out on a Fisons EA-1108 microanalyser. IR spectra were recorded from KBr discs (4000–400 cm⁻¹) with a Bruker IFS28FT spectrophotometer.

3.2. Synthesis of the Precursor 1_{∞} [Zn(chel)(H₂O)₂]

 1_{oc} [Zn(chel)(H₂O)₂] [4] was obtained by reaction of ZnCO₃ and chelidonic acid (1:1 molar ratio) in methanol. The resulting suspension was heated under reflux for 2 h and stirred at room temperature for 1 day. The colourless solid was filtered off, washed with MeOH and vacuum dried.

3.3. Synthesis of the Complexes

3.3.1. ²_∞[Zn(chel)(4,4-bipy)(H₂O)]·2H₂O (1)

Colourless single crystals of **1** were obtained by slow diffusion of a solution of 1_{∞} [Zn(chel)(H₂O)₂] (0.20 mmol) in water and a solution of 4,4'-bipyridine (4,4-bipy, 0.20 mmol) in ethanol.

Data. Anal. calc. for C17H16O9N2Zn (457.7): C 44.7, H 3.5, N 6.1%; Found: C 44.5, H 3.4, N 5.7%. IR (KBr, cm⁻¹): 3446m,b; 1640vs; 1407m; 1360s.

3.3.2. ¹_∞[Zn(4,4-bipy)(H₂O)₄]chel·3H₂O (2)

Compound **2** was obtained as colourless single crystals by slow evaporation of the resulting solution after filtering off the crystals of **1**.

Data. Anal. calc. for C₁₇H₂₄O₁₃N₂Zn (529.8): C 38.6, H 4.6, N 5.3%; Found: C 38.5, H 4.9, N 5.4%. IR (KBr, cm⁻¹): 3444m,b; 1641vs; 1416m; 1361s.

3.3.3. ²_∞[Zn(chel)(bpe)(H₂O)]·H₂O (3)

Compound **3** was also obtained as colourless single crystals by slow diffusion of a solution of 1_{∞} [Zn(chel)(H₂O)₂] (0.20 mmol) in water and a solution of 1,2-bis(4-pyridyl)ethane (bpe, 0.20 mmol) in ethanol.

Data. Anal. calc. for C19H18O8N2Zn (467.7): C 48.9, H 3.9, N 6.0%; Found: C 48.1, H 4.0, N 5.8%. IR (KBr, cm⁻¹): 3365m,b ; 1635vs; 1425m; 1355s.

3.3.4. 1. [Cu(4,4-bipy)(H2O)4]chel·3H2O (4a) and 1. [Cu(4,4-bipy)(H2O)4]chel·6H2O (4b)

A solution of 4,4'-bipyridine (0.156 g, 1 mmol) in methanol (10 mL) was slowly added to a solution of Cu(NO₃)₂·2.5H₂O (0.233 g, 1 mmol) in water (10 mL). The mixture was heated under reflux for 1 h and was left to cool down to room temperature. A solution of chelidonic acid (0.184 g, 1 mmol) and KOH (0.112 g, 2 mmol) in 2:1 MeOH/H₂O was added to the mixture, which was then heated under reflux for 1 h and was left to cool down to room temperature. The blue precipitate was filtered off and dissolved in water. Blue crystals of **4a** were obtained by slow evaporation of the aqueous solution. After separation of the crystals of **4a** the slow evaporation of the remaining solution gave rise to some brown crystals of **4b**.

Data for 4a: Anal. calc. for C17H24O13N2Cu (527.9): C 38.7, H 4.6, N 5.3%; Found: C 39.1, H 4.1, N 5.2%. IR (KBr, cm⁻¹): 3445s,b; 1637vs, 1404m, 1358m.

Data for **4b**: Anal. calc. for C₁₇H₃₀O₁₆N₂Cu (581.1): C 35.1, H 5.2, N 4.8%; Found: C 35.5, H 5.4, N 5.0%. IR (KBr, cm⁻¹): 3420s,b; 1613vs, 1403m, 1354s.

3.4. Crystallography

Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer using graphite monochromated Mo-K α radiation (λ = 0.71073 Å). All data were corrected

for Lorentz and polarisation effects. The frames were integrated with the Bruker Saint software package [32] and the data were corrected for absorption using the program SADABS. [33] The structures were solved by direct methods using the program SHELXS97 [34]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the programme SHELXL97 [34] or the programme SHELXL [35] with OLEX2 [36]. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. The hydrogen atoms of the water molecules were located from a difference Fourier map and refined with isotropic parameters but the hydrogen atoms for the crystallisation water molecules in 1 could not be located. Compound 4a crystallised in the chiral space group *P*2*i*2*i*2 and its absolute configuration was confirmed by a value of 0.010(6) for the Flack parameter [37]. Drawings were produced with MERCURY [38]. Crystal data and structure refinement parameters are reported in Table S5.

4. Conclusions

The study described here concerned the crystalline species resulting from chelidonic acid/4,4'-bipyridine or 1,2-bis(4-pyridyl)ethane/Zn(II) or Cu(II) systems in aqueous solutions. The process led to the isolation of single crystals of two kinds of coordination polymers; the 1D Zn(II) and Cu(II) cationic polymers (**2**, **4a** and **4b**) with the chelidonate anion in the second coordination sphere and the 2D Zn(II) polymers (**1** and **3**) with the bridging chelidonate ligand showing a new coordination mode, $\mu(\kappa^2O^{III}.O^{IV}:\kappa O^V)$. The results highlight the ability of chelidonate to stabilise different coordination compounds through its participation in the first or second coordination sphere. This feature is evidenced by the formation of ${}^2_{\infty}$ [Zn(chel)(4,4-bipy)(H₂O)]·2H₂O (**1**) and ${}^1_{\infty}$ [Zn(4,4-bipy)(H₂O)₄]chel·3H₂O (**2**) from the same reaction by diffusion. The crystallisation of three compounds containing the 1D [M(4,4-bipy)(H₂O)₄]²⁺ (M = Zn, Cu) indicates the great stability of this cationic polymer, which was confirmed by a CSD search as the one included in Section 2.1. of this paper.

The five coordination polymers crystallise as hydrates but the crystallisation water molecules play different roles in the neutral polymers and in the solids containing the cationic polymers. In the neutral compounds the water molecules are weakly hydrogen bonded to the metal-organic framework but in the compounds based on the cationic polymers, the water molecules play a key role in the formation of the resulting supramolecular networks. These latter compounds are hydrogen-bonded networks through the second coordination sphere, which is organised in $[(H_2O)_n chel]^{2-}$ (n = 3 or 6) layers.

The presence of non-associated water molecules (W1 motif) is common in the networks for all of the compounds reported here. Furthermore, in all compounds a recurrent supramolecular synthon based on the interaction between a water molecule (coordinated in the neutral compounds and free in the cationic species) and the two carboxylate groups of a chelidonate anion (coordinated or not) is observed. This synthon leads to the formation of an eight-membered ring in all cases.

From the point of view of crystal engineering the biological anion chelidonate, in combination with N,N'-bridging ligands, is an interesting tool to obtain coordination polymers and/or hydrogen-bonded networks.

Supplementary Materials: The following are available online at www.mdpi.com//3/1/19/s1, Figure S1: Infrared spectra, Table S1: Selected bond lengths/Å and angles/° in the cationic polymers [Zn(4,4-bipy)(H₂O)₄](chel)·3H₂O (2), [Cu(4,4-bipy)(H₂O)₄](chel)·3H₂O (4a) and [Cu(4,4-bipy)(H₂O)₄](chel)·6H₂O (4b), Table S2: Selected bond lengths/Å and angles/° in the neutral polymers ${}^{2}_{\infty}$ [Zn(chel)(4,4-bipy)(H₂O)]·2H₂O (1) and ${}^{2}_{\infty}$ [Zn(chel)(bpe)(H₂O)]·H₂O (3), Table S3: Main hydrogen bonds in the cationic polymers [Cu(4,4-bipy)(H₂O)₄](chel)·3H₂O (4a) [Cu(4,4-bipy)(H₂O)₄](chel)·6H₂O (4b) and [Zn(4,4-bipy)(H₂O)₄](chel)·3H₂O (2), Table S4: Main hydrogen bonds in the neutral polymers ${}^{2}_{\infty}$ [Zn(chel)(4,4-bipy)(H₂O)₄](chel)·6H₂O (4b) and [Zn(4,4-bipy)(H₂O)₄](chel)·3H₂O (2), Table S4: Main hydrogen bonds in the neutral polymers ${}^{2}_{\infty}$ [Zn(chel)(4,4-bipy)(H₂O)₄](chel)·6H₂O (1) and ${}^{2}_{\infty}$ [Zn(chel)(bpe)(H₂O)]·H₂O

(3), Table S5: Crystal data and structure refinement. CCDC entries 2051289–2051293 contain the supplementary crystallographic data for 1, 2, 3, 4a and 4b.

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Sample Availability: Samples of the compounds are available from the authors.

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