

Article

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

Rosa Carballo ^{1,*}, Ana Belén Lago ^{2,*}, Arantxa Pino-Cuevas ¹, Olaya Gómez-Paz ¹, Nuria Fernández-Hermida ¹ and Ezequiel M. Vázquez-López ¹

¹ Departamento de Química Inorgánica, Instituto de Investigación Sanitaria Galicia Sur (IISGS), Universidade de Vigo, 36310 Vigo, Spain; aripc-27@hotmail.com (A.P.-C.); olgomez@uvigo.es (O.G.-P.); grupo_qi5@uvigo.es (N.F.-H.); ezequiel@uvigo.gal (E.M.V.-L.)

² Departamento de Química, Facultad de Ciencias, Sección Química Inorgánica, Universidad de la Laguna, 38206 La Laguna, Spain

* Correspondence: rcrial@uvigo.es (R.C.); alagobla@ull.edu.es (A.B.L.)

Abstract: The biomolecule chelidonic acid (H_2chel , 4-oxo-4H-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 $^1_\infty[Zn(4,4-bipy)(H_2O)_4]chel \cdot 3H_2O$ (**2**) and in the two pseudopolymorphic $^1_\infty[Cu(4,4-bipy)(H_2O)_4]chel \cdot nH_2O$ ($n = 3$, **4a**; $n = 6$, **4b**), and the 2D neutral coordination polymers $^2_\infty[Zn(chel)(4,4-bipy)(H_2O)] \cdot 2H_2O$ (**1**) and $^2_\infty[Zn(chel)(bpe)(H_2O)] \cdot H_2O$ (**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; metallocsupramolecular compounds; H-bonding pattern; X-ray diffraction



Citation: Carballo, R.; Lago, A.B.; Pino-Cuevas, A.; Gómez-Paz, O.; Fernández-Hermida, N.; Vázquez-López, E.M. Neutral and Cationic Chelidonate Coordination Polymers with N,N' -Bridging Ligands. *Chemistry* **2021**, *3*, 256–268. <https://doi.org/10.3390/chemistry3010019>

Received: 9 January 2021

Accepted: 7 February 2021

Published: 11 February 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



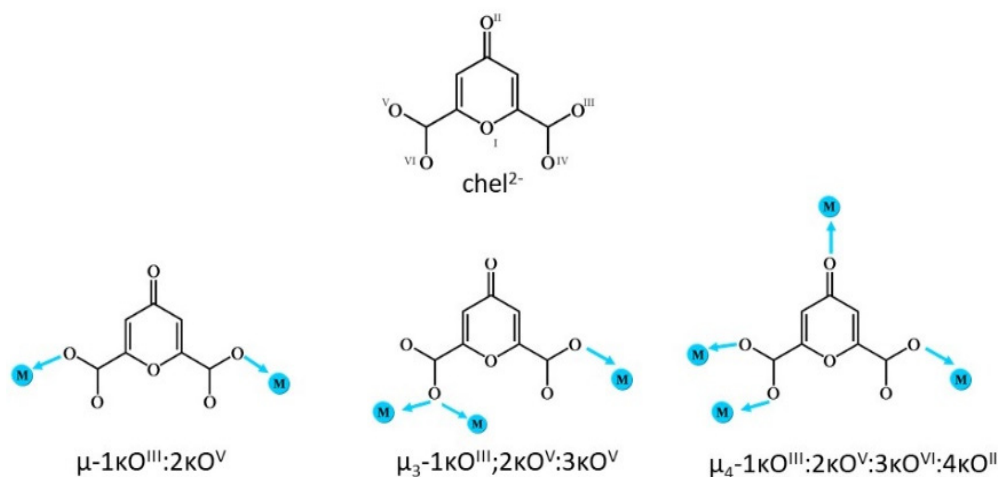
Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Chelidonic acid (H_2chel , 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, H_2chel 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, $chel^{2-}$ 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 metallocsupramolecular 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), 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 ${}^2_{\infty}[\text{Cu}(\text{chel})(\text{bipy})]$ [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,N'*-ligands 4,4'-bipyridine (4,4'-bipy) and 1,2-bis(4-pyridyl)ethane (bpe), which can facilitate the extension of the metal-ligand 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 ${}^2_{\infty}[\text{Zn}(\text{chel})(4,4\text{-bipy})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (1) and ${}^2_{\infty}[\text{Zn}(\text{chel})(\text{bpe})(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$ (3), in which the chelidonate anion acts as a bridging ligand. The cationic 1D coordination polymer ${}^1_{\infty}[\text{Zn}(4,4\text{-bipy})(\text{H}_2\text{O})_4]\text{chel}\cdot 3\text{H}_2\text{O}$ (2) and its analogues ${}^1_{\infty}[\text{Cu}(4,4\text{-bipy})(\text{H}_2\text{O})_4]\text{chel}\cdot n\text{H}_2\text{O}$ ($n = 3$, 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 ${}^1_{\infty}[\text{Zn}(\text{chel})(\text{H}_2\text{O})_2]$ [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 ${}^2_{\infty}[\text{Zn}(\text{chel})(4,4\text{-bipy})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (1) and ${}^2_{\infty}[\text{Zn}(\text{chel})(\text{bpe})(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$ (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 ${}^1_{\infty}[\text{Zn}(4,4\text{-bipy})(\text{H}_2\text{O})_4]\text{chel}\cdot 3\text{H}_2\text{O}$ (2), with the uncoordinated chelidonate anion, were isolated. Polymer 2 contains the ${}^1_{\infty}[\text{Zn}(4,4\text{-bipy})(\text{H}_2\text{O})_4]^{2+}$ 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 ${}^1_{\infty}[\text{M}(4,4\text{-bipy})(\text{H}_2\text{O})_4]^{2+}$ is observed for other metal centres in the presence of differ-

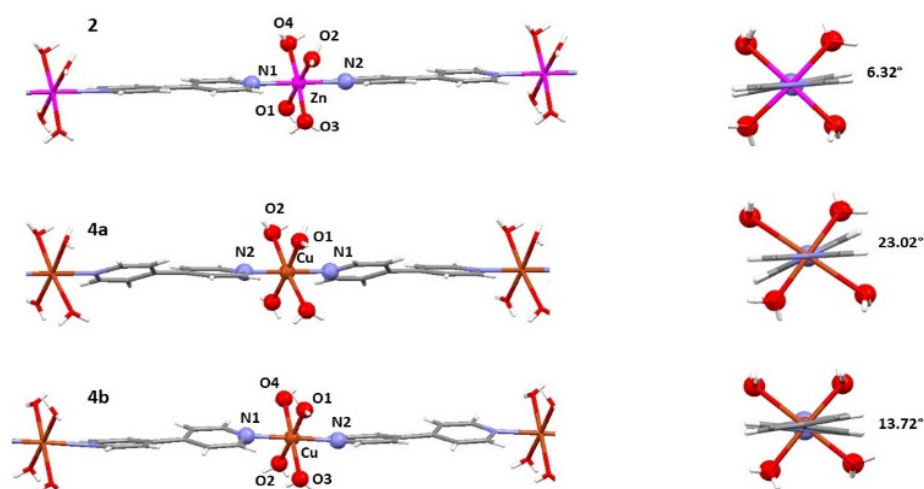


Figure 1. Cationic chains in coordination polymers **2**, **4a** and **4b** showing in detail the coordination environment and the disposition of the 4,4-bipy rings.

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

	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) 2.195(2)	2.049(3) 2.031(3)	2.093(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)

The three structures are polymeric chains based on the cationic complexes $[M(4,4\text{-bipy})(\text{OH}_2)_4]^{2+}$ ($M = \text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$), where the N-donor ligands act as a bridge between the metal centres. The second coordination spheres are formed by dianionic chelidionate anions and three or six water molecules. Complexes **4a** and **4b** crystallise in the orthorhombic chiral $P2_12_12$ 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.

All M^{II} metal centres are $[\text{N}_2\text{O}_4]$ -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 ($\text{Cu}-\text{O}_{\text{water}}$ and $\text{Cu}-\text{N}$ 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 chelidionate 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 $O_{\text{chelidonate}} \cdots O_{\text{water}}$ 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, O_{2w} , and two chelidonate anions form a discrete dimer through H-bonding interactions to yield a four-membered ring, with $O \cdots O$ distances of 2.781 and 2.932 Å (Figure 2, Table S3). Another crystallisation water molecule, O_{1w} , 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.

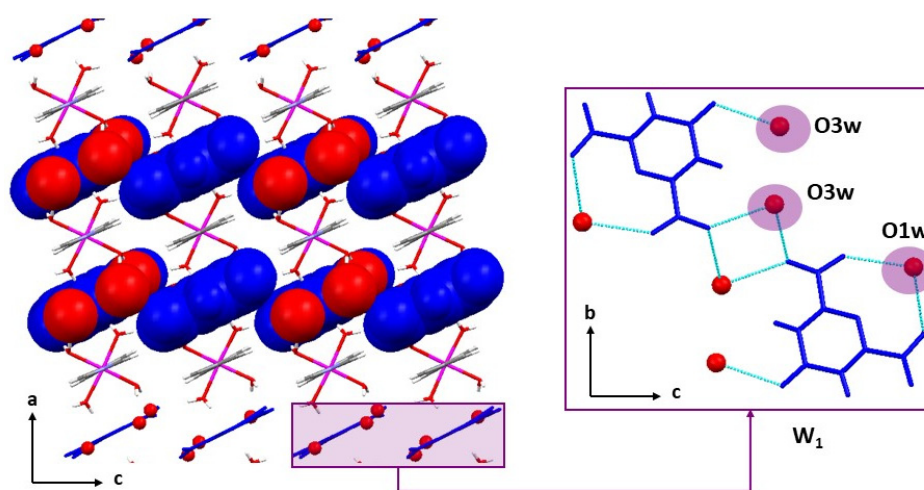


Figure 2. Supramolecular arrangement of **2** showing in detail the interactions established between the crystallisation water molecules and chelidonate anions.

The cationic chains of **2** are anchored to these water-chelidonate dimers through $O_{W_{\text{coord}}} \cdots O_{\text{carboxy}}$ and $O_{W_{\text{coord}}} \cdots O_{W_{\text{crystallisation}}}$ 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 $[(H_2O)_n\text{chel}]^{2-}$ sheets. In this way, the layers act as the ‘glue’ between the cationic units to form the final metallocsupramolecular arrangements [30]. This kind of 2D anion-water association has been observed in other cases, such as $[Ni(4,4\text{-bipy})(H_2O)_4] \cdot 0.5(\text{btc}) \cdot H_2O$ ($H_4\text{btc}$, 1,2,4,5-benzenetetracarboxylic acid) [25].

In **4a** the crystallisation water molecules are also not interconnected by hydrogen bonds (W_1 motif) and only one of them (O_{2w}) is involved in the formation of the supramolecular $[(H_2O)_3\text{chel}]^{2-}$ layer (Figure 3), with $O \cdots O$ 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).

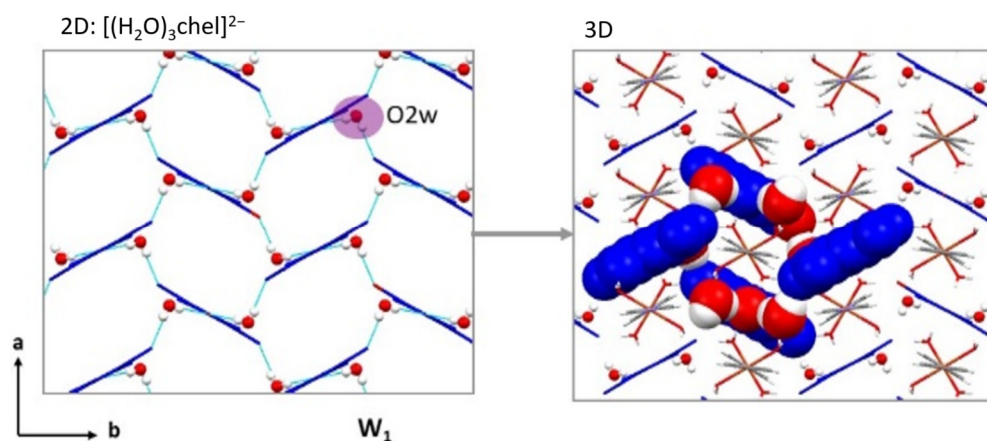


Figure 3. Supramolecular arrangement of **4a** showing in detail the layers formed by the interaction of crystallisation water molecules and chelidonate anions.

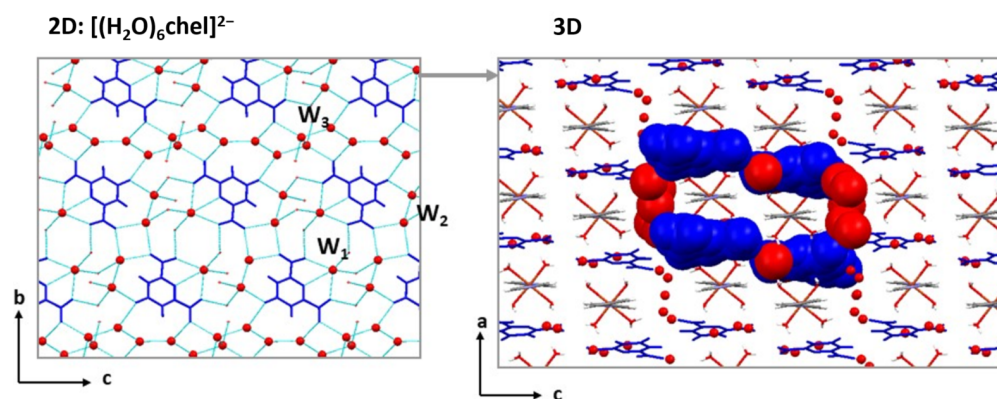


Figure 4. Supramolecular arrangement of **4b** showing in detail the layer formed by the interaction of crystallisation water molecules and chelidonate anions.

In **4b** the six water molecules of crystallisation have three different arrangements, namely one isolated molecule (W_1), a dimer (W_2) and a trimer (W_3) (Figure 4). The isolated molecule, O_{13w} , corresponds to the W_1 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 ($O\cdots O$ 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 (W_2) with an $O\cdots O$ distance of 2.855(4) Å and in a trimer (W_3) with shorter $O\cdots O$ 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 $[(H_2O)_6chel]^{2-}$ ladder-shaped layers (Figure 4) that leave space to accommodate the cationic units anchored through $O_{w_{coord}} \cdots O_{carboxy}$ and $O_{w_{coord}} \cdots O_{w_{crystallisation}}$ interactions.

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**.

2.4. Crystal Structures of Neutral Polymers **1** and **3**

The Zn(II) polymeric compounds **1** and **3** crystallise in the $P-1$ and $P2_1/c$ space groups, respectively. The significant structural parameters are listed in Table S2 and a summary of bond lengths/Å and angles/ $^\circ$ 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).

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**).

	1	3
Zn–O(1W)	2.032(3)	2.158(2)
Zn–Ochel	2.015(3)	1.978(2)
	2.539(3)	2.557(2)
	2.130(3)	2.085(2)
Zn–N	2.151(4)	2.147(2)
	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)°

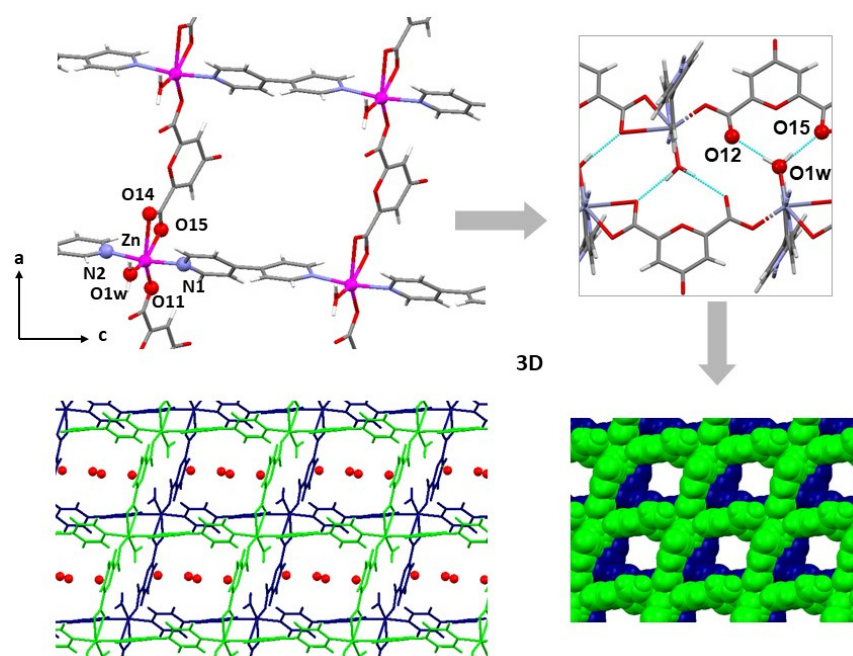


Figure 5. View of the 2D layers of ${}^2\infty$ [Zn(chel)(4,4-bipy)(H₂O)]·2H₂O (**1**) and the final 3D supramolecular arrangement, showing the zinc atom environment and the corresponding labelling scheme.

Chelidonate acts in both structures as a bridging ligand in a μ -1 κ^2 O^{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.

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–O_W 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.

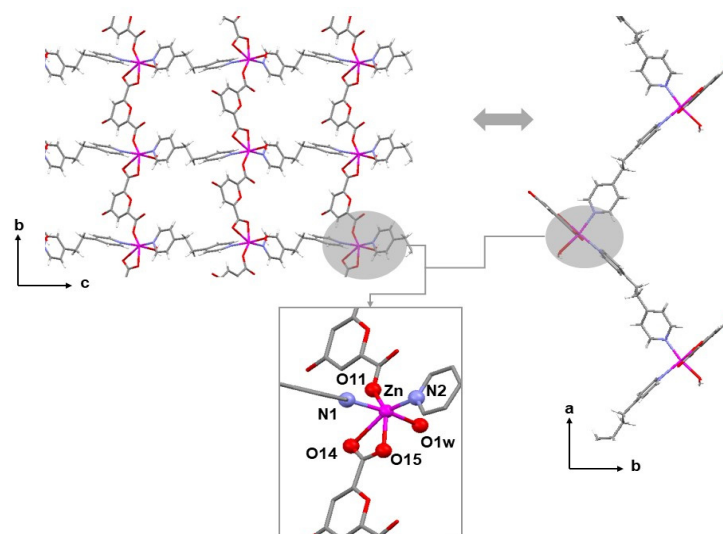
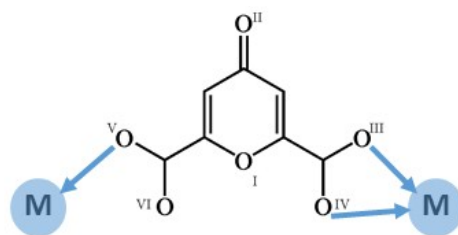


Figure 6. Structure of $[\text{Zn}(\text{chel})(\text{bpe})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (**3**) showing the zinc atom environment and the corrugated disposition of the layers.



Scheme 3. New coordination mode, $\mu\text{-}1\kappa^2\text{O}^{\text{III}},\text{O}^{\text{IV}}:2\kappa\text{O}^{\text{V}}$, of chelidonate in coordination polymers **1** and **3**.

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 $11.35 \times 9.93 \text{ \AA}$ and angles of 97° and 82° (defined by $\text{Zn}\cdots\text{Zn}$ distances and $\text{Zn}\cdots\text{Zn}\cdots\text{Zn}$ 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 $13.43 \times 9.61 \text{ \AA}$ and angles of 97° and 82° .

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 $\text{C}\text{-CH}_2\text{-CH}_2\text{-C}$) 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 ($d(\text{O1W} \cdots \text{Ochel}) = 2.699(4)$ and $2.772(5) \text{ \AA}$; 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 ($d(\text{O1W} \cdots \text{Ochel}) = 2.762(3)$ and $2.825(3) \text{ \AA}$, 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 ($d(\text{Ow} \cdots \text{O}) = 3.125(5) \text{ \AA}$).

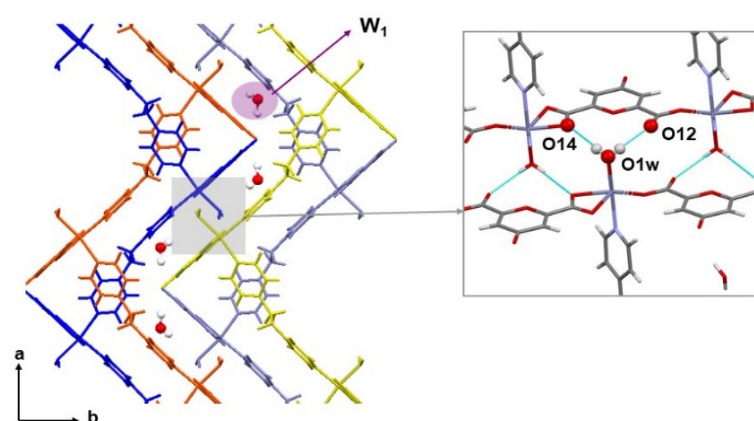


Figure 7. View of the 3D supramolecular arrangement in $[\text{Zn}(\text{chel})(\text{bpe})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (**3**) showing details of the of $\text{O1w}-\text{H1w}\cdots\text{O}$ hydrogen-bonding interactions.

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**.

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 ($4000\text{--}400\text{ cm}^{-1}$) with a Bruker IFS28FT spectrophotometer.

3.2. Synthesis of the Precursor $^1_\infty[\text{Zn}(\text{chel})(\text{H}_2\text{O})_2]$

$^1_\infty[\text{Zn}(\text{chel})(\text{H}_2\text{O})_2]$ [4] was obtained by reaction of ZnCO_3 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. $^2_\infty[\text{Zn}(\text{chel})(4,4\text{-bipy})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (**1**)

Colourless single crystals of **1** were obtained by slow diffusion of a solution of $^1_\infty[\text{Zn}(\text{chel})(\text{H}_2\text{O})_2]$ (0.20 mmol) in water and a solution of 4,4'-bipyridine (4,4-bipy, 0.20 mmol) in ethanol.

Data. Anal. calc. for $\text{C}_{17}\text{H}_{16}\text{O}_9\text{N}_2\text{Zn}$ (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}): 3446 m,b; 1640 vs; 1407 m; 1360 s.

3.3.2. $^1_\infty[\text{Zn}(4,4\text{-bipy})(\text{H}_2\text{O})_4]\text{chel}\cdot 3\text{H}_2\text{O}$ (**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 $\text{C}_{17}\text{H}_{24}\text{O}_{13}\text{N}_2\text{Zn}$ (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}): 3444 m,b; 1641 vs; 1416 m; 1361 s.

3.3.3. $^2_\infty[\text{Zn}(\text{chel})(\text{bpe})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (**3**)

Compound **3** was also obtained as colourless single crystals by slow diffusion of a solution of $^1_\infty[\text{Zn}(\text{chel})(\text{H}_2\text{O})_2]$ (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 $\text{C}_{19}\text{H}_{18}\text{O}_8\text{N}_2\text{Zn}$ (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}): 3365 m,b; 1635 vs; 1425 m; 1355 s.

3.3.4. $^1\infty[\text{Cu}(4,4\text{-bipy})(\text{H}_2\text{O})_4]\text{chel}\cdot 3\text{H}_2\text{O}$ (4a) and $^1\infty[\text{Cu}(4,4\text{-bipy})(\text{H}_2\text{O})_4]\text{chel}\cdot 6\text{H}_2\text{O}$ (4b)

A solution of 4,4'-bipyridine (0.156 g, 1 mmol) in methanol (10 mL) was slowly added to a solution of $\text{Cu}(\text{NO}_3)_2\cdot 2.5\text{H}_2\text{O}$ (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/ H_2O 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 $\text{C}_{17}\text{H}_{24}\text{O}_{13}\text{N}_2\text{Cu}$ (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}): 3445 s,b; 1637 vs, 1404 m, 1358 m.

Data for **4b**: Anal. calc. for $\text{C}_{17}\text{H}_{30}\text{O}_{16}\text{N}_2\text{Cu}$ (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}): 3420 s,b; 1613 vs, 1403 m, 1354 s.

3.4. Crystallography

Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). 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 $P2_12_12$ 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, $\mu(\kappa^2\text{O}^{\text{III}}\cdot\text{O}^{\text{IV}}:\kappa\text{O}^{\text{V}})$. 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 $^2\infty[\text{Zn}(\text{chel})(4,4\text{-bipy})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (**1**) and $^1\infty[\text{Zn}(4,4\text{-bipy})(\text{H}_2\text{O})_4]\text{chel}\cdot 3\text{H}_2\text{O}$ (**2**) from the same reaction by diffusion. The crystallisation of three compounds containing the 1D $[\text{M}(4,4\text{-bipy})(\text{H}_2\text{O})_4]^{2+}$ ($\text{M} = \text{Zn}, \text{Cu}$) 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 $[(\text{H}_2\text{O})_n\text{chel}]^{2-}$ ($n = 3$ 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 <https://www.mdpi.com/2624-8549/3/1/19/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_∞[Zn(chel)(4,4-bipy)(H₂O)]·2H₂O (1) and ²_∞[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_∞[Zn(chel)(4,4-bipy)(H₂O)]·2H₂O (1) and ²_∞[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.

Author Contributions: Conceptualization, R.C. and A.B.L.; methodology, R.C., A.P.-C. and O.G.-P.; synthesis, characterisation, thermal analysis A.P.-C. and N.F.-H.; formal analysis, R.C., A.P.-C. and O.G.-P.; investigation, O.G.-P.; resources, R.C. and O.G.-P.; writing—original draft preparation, R.C. and A.B.L.; writing—review and editing, R.C., A.B.L. and E.M.V.-L.; visualization, R.C. and A.B.L.; supervision, E.M.V.-L.; project administration, R.C. and E.M.V.-L.; funding acquisition, R.C. and E.M.V.-L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministerio de Ciencia e Innovación (Spain) (research project PID2019-110218RB-I00).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in the article and in the Supplementary Materials.

Acknowledgments: SC-XRD measurements were performed at the Unidade de Difracción de Raios X de Monocristal (CACTI-Universidade de Vigo), Spain. O.G.P. thanks the Xunta de Galicia for a predoctoral contract.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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

References

1. Kumar Singh, D.; Gulati, K.; Ray, A. Effects of chelidonic acid, a secondary plant metabolite, on mast cell degranulation and adaptive immunity in rats. *Int. Immunopharmacol.* **2016**, *40*, 229–234. [[CrossRef](#)] [[PubMed](#)]
2. Kim, D.-S.; Kim, S.-J.; Kim, M.-C.; Jeon, Y.-D.; Um, J.-Y.; Hong, S.-H. The Therapeutic Effect of Chelidonic Acid on Ulcerative Colitis. *Biol. Pharm. Bull.* **2012**, *35*, 666–671. [[CrossRef](#)]
3. Jeong, H.-J.; Yang, S.-Y.; Kim, H.-Y.; Kim, N.-R.; Jang, J.-B.; Kim, H.-M. Chelidonic acid evokes antidepressant-like effect through the up-regulation of BDNF in forced swimming test. *Exp. Biol. Med.* **2016**, *241*, 1559–1567. [[CrossRef](#)]
4. Zhou, X.-X.; Liu, M.-S.; Lin, X.-M.; Fang, H.-C.; Chen, J.-Q.; Yang, D.-Q.; Cai, Y.-P. Construction of three low dimensional Zn(II) complexes based on different organic-carboxylic acids. *Inorg. Chim. Acta* **2009**, *362*, 1441–1447. [[CrossRef](#)]
5. Yasodha, V.; Govindarajan, S.; Lowb, J.N.; Glidewell, C. Cationic, neutral and anionic metal(II) complexes derived from 4-oxo-4H-pyran-2,6-dicarboxylic acid (chelidonic acid). *Acta Cryst.* **2007**, *63*, m207–m215.

6. Fainerman-Melnikova, M.; Clegg, J.K.; Pakchung, A.A.H.; Jensen, P.; Codd, R. Structural diversity of complexes between Cu(II) or Ni(II) and endocyclic oxygen- or nitrogen-containing ligands: Synthesis, X-ray structure determinations and circular dichroism spectra. *Cryst. Eng. Comm.* **2010**, *12*, 4217–4225. [[CrossRef](#)]
7. Fang, M.; Chang, L.; Liu, X.; Zhao, B.; Zuo, Y.; Chen, Z. Fabrication and Properties of Eight Novel Lanthanide–Organic Frameworks Based on 4-Hydroxypyran-2,6-dicarboxylate and 4-Hydroxypyridine-2,6-dicarboxylate. *Cryst. Growth Des.* **2009**, *9*, 4006–4016. [[CrossRef](#)]
8. Zhang, Z.-J.; Zhang, S.-Y.; Li, Y.; Niu, Z.; Shi, W.; Cheng, P. Systematic investigation of the lanthanide coordination polymers with γ -pyrone-2,6-dicarboxylic acid. *Cryst. Eng. Comm.* **2010**, *12*, 1809–1815. [[CrossRef](#)]
9. Qu, B.-T.; Lai, J.-C.; Liu, S.; Liu, F.; Gao, Y.-D.; You, X.-Z. Cu- and Ag-Based Metal–Organic Frameworks with 4-Pyranone-2,6-dicarboxylic Acid: Syntheses, Crystal Structures, and Dielectric Properties. *Cryst. Growth Des.* **2015**, *15*, 1707–1713. [[CrossRef](#)]
10. Yasodha, V.; Govindarajan, S.; Starosta, W.; Leciejewicz, J. New Metal–Organic Framework Solids Built from Barium and Isoelectronic Chelidamic and Chelidonic Acids. *J. Chem. Crystallogr.* **2011**, *41*, 1988–1997. [[CrossRef](#)]
11. Eubank, J.F.; Kravtsov, V.C.; Eddaoudi, M. Synthesis of Organic Photodimeric Cage Molecules Based on Cycloaddition via Metal–Ligand Directed Assembly. *J. Am. Chem. Soc.* **2007**, *129*, 5820–5821. [[CrossRef](#)] [[PubMed](#)]
12. Lago, A.B.; Carballo, R.; Fernández-Hermida, N.; Rodríguez-Hermida, S.; Vázquez-López, E.M. Coordination polymers with chelidonate (4-oxo-4H-pyran-2,6-dicarboxylate) anions and dmsO: [Zn(chel)(dmsO)₂] and linkage isomers of [Co(chel)(dmsO)(OH₂)₃]-H₂O. *J. Mol. Struct.* **2011**, *1003*, 121–128. [[CrossRef](#)]
13. Lago, A.B.; Carballo, R.; Fernández-Hermida, N.; Vázquez-López, E.M. Mononuclear discrete complexes and coordination polymers based on metal(II) chelidonate complexes with aromatic *N,N*-chelating ligands. *CrystEngComm.* **2011**, *13*, 941–951. [[CrossRef](#)]
14. Carlucci, L.; Ciani, G.; Proserpio, D.M.; Sironi, A. Extended networks via hydrogen bond cross-linkages of [M(bipy)] (M = Zn²⁺ or Fe²⁺; bipy = 4,4′-bipyridyl) linear co-ordination polymers. *J. Chem. Soc. Dalton Trans.* **1997**, 1801–1804. [[CrossRef](#)]
15. Lian, Z.-X.; Cai, J.; Chen, C.-H. A series of metal-organic frameworks constructed with arenesulfonates and 4,4′-bipy ligands. *Polyhedron* **2007**, *26*, 2647–2654. [[CrossRef](#)]
16. Zhang, J.; Zhu, L.-G. Syntheses, structures, and supra-molecular assemblies of zinc 4-sulfobenzoate complexes with chelating and/or bridging ligands. *J. Mol. Struct.* **2009**, *931*, 87–93. [[CrossRef](#)]
17. Xiong, W.; Su, Y.; Zhang, Z.; Chen, Z.; Liang, F.; Wang, L. Synthesis and Crystal Structures of Two Metal Complexes Formed in the Solvothermal Decomposition Reactions of *N*-Carboxyphenylenesulfonyl-*S*-Carboxymethyl-L-Cysteine. *J. Chem. Cryst.* **2011**, *41*, 1510–1514. [[CrossRef](#)]
18. Mao, H.; Zhang, C.; Li, G.; Zhang, H.; Hou, H.; Li, L.; Wu, Q.; Zhu, Y.; Wang, E. New types of the flexible self-assembled metal–organic coordination polymers constructed by aliphatic dicarboxylates and rigid bidentate nitrogen ligands. *Dalton Trans.* **2004**, 22, 3918–3925. [[CrossRef](#)]
19. García, H.C.; Diniz, R.; Yoshida, M.I.; de Oliveira, L.F.C. Synthesis, structural studies and vibrational spectroscopy of Fe²⁺ and Zn²⁺ complexes containing 4,4′-bipyridine and barbiturate anion. *J. Mol. Struct.* **2010**, *978*, 79–85. [[CrossRef](#)]
20. Colinas, R.; Rojas-Andrade, M.D.; Chakraborty, I.; Oliver, S.R.J. Two structurally diverse Zn-based coordination polymers with excellent antibacterial activity. *CrystEngComm.* **2018**, *20*, 3353–3362. [[CrossRef](#)]
21. *CSD Web Interface–Intuitive, Cross-Platform, Web-Based access to CSD Data*; Cambridge Crystallographic Data Centre: Cambridge, UK, 2017.
22. Wang, Y.; Feng, L.; Li, Y.; Hu, C.; Wang, E.; Hu, N.; Jia, H. Novel hydrogen-bonded three-dimensional networks encapsulating one-dimensional covalent chains: [M(4,4′-bipy)(H₂O)₄](4-abs)₂nH₂O (4,4′-bipy = 4,4′-bipyridine; 4-abs = 4-aminobenzenesulfonate) (M = Co, n = 1; M = Mn, n = 2). *Inorg. Chem.* **2002**, *41*, 6351–6357. [[CrossRef](#)] [[PubMed](#)]
23. Manna, S.C.; Ghosh, A.K.; Zangrando, E.; Ray Chaudhuri, N. 3D supramolecular networks of Co(II)/Fe(II) using the croconate dianion and a bipyridyl spacer: Synthesis, crystal structure and thermal study. *Polyhedron* **2007**, *26*, 1105–1112. [[CrossRef](#)]
24. Elahi, S.M.; Chand, M.; Deng, W.-H.; Pal, A.; Das, M.C. Polycarboxylate-Templated Coordination Polymers: Role of Templates for Superprotonic Conductivities of up to 10^{−1} S cm^{−1}. *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 6662–6666. [[CrossRef](#)]
25. Wang, X.-L.; Qin, C.; Wang, E.-B. Polythreading of Infinite 1D Chains into Different Structural Motifs: Two Poly(pseudo-rotaxane) Architectures Constructed by Concomitant Coordinative and Hydrogen Bonds. *Cryst. Growth Des.* **2006**, *6*, 439–443. [[CrossRef](#)]
26. Kanoo, P.; Gurunatha, K.L.; Maji, T.K. Temperature-Controlled Synthesis of Metal–Organic Coordination Polymers: Crystal Structure, Supramolecular Isomerism, and Porous Property. *Cryst. Growth Des.* **2009**, *9*, 4147–4156. [[CrossRef](#)]
27. García, H.C.; Diniz, R.; Yoshidab, M.I.; de Oliveira, L.F.C. An intriguing hydrogen bond arrangement of polymeric 1D chains of 4,4′-bipyridine coordinated to Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ ions having barbiturate as counterions in a 3D network. *CrystEngComm.* **2009**, *11*, 881–888. [[CrossRef](#)]
28. Fei, H.; Oliver, S.R.J. Two cationic metal–organic frameworks based on cadmium and α,ω -alkanedisulfonate anions and their photoluminescent properties. *Dalton Trans.* **2010**, 39, 11193–11200. [[CrossRef](#)]
29. Robin, A.Y.; Fromm, K.M. Coordination polymer networks with *O*- and *N*-donors: What they are, why and how they are made. *Coord. Chem. Rev.* **2006**, *250*, 2127–2157. [[CrossRef](#)]
30. Carballo, R.; Covelo, B.; García-Martínez, E.; Lago, A.B.; Vázquez-López, E.M. Role of inorganic and organic anions in the formation of metallosupramolecular assemblies of silver(I) coordination polymers with the twisted ligand bis(4-pyridylthio)methane. *Polyhedron* **2009**, *5*, 923–932. [[CrossRef](#)]

31. Kitaigorodskii, A.I. *Molecular Crystals and Molecules*; Academic Press: New York, NY, USA, 1973.
32. Siemens SAINT. *Version 4, Software Reference Manual*; Siemens Analytical X-Ray Systems, Inc.: Madison, WI, USA, 1996.
33. Sheldrick, G.M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1997.
34. Sheldrick, G.M. *SHELXS-97 and SHELXL-97, Program for Crystal Structure Solution and Refinement*; University of Göttingen: Göttingen, Germany, 1997.
35. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.
36. Dolomanov, V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341. [[CrossRef](#)]
37. Flack, H.D. On enantiomorph-polarity estimation. *Acta Cryst.* **1983**, *39*, 876–881. [[CrossRef](#)]
38. Bruno, J.; Cole, J.C.; Edgington, P.R.; Kessler, M.K.; Macrae, C.F.; McCabe, P.; Pearson, J.; Taylor, R. MERCURY. New Software for Visualizing Crystal Structures. *Acta Cryst.* **2002**, *B58*, 389. [[CrossRef](#)] [[PubMed](#)]