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Two 3D supramolecular architectures from zinc hydrogen aconitate 1D polymers

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Abstract

The reaction of $Zn(NO_3)_2 \cdot 3(H_2O)$ with *trans*-aconitic acid, in presence of chelating Lewis bases, leads to the formation of the 1D polymers $[Zn(N–N)(LH)] \cdot nH_2O$, where LH_3 = *trans*-aconitic acid, **1** : N–N = 1,10-phenanthroline (phen), $n = 1$, **2** : N–N = 2,2′-bipyridine (bpy), $n = 2$. 3D supramolecular assemblies are constructed through H-bonding and stacking interactions.

Keywords: Zinc(II); 1D polymer; 3D supramolecular architecture; H-bond; Stacking; Crystal structure

Metal-organic polymer chemistry is a research topic that increasingly attracts researchers' interest due to the variety of the composition and topology of the produced compounds, and also to their interesting functional properties and potential applications. Despite the successful efforts of several research groups to design the topology of certain metal-organic frameworks, it remains more of an art than a science, since most of the new polymeric compounds are synthesized through self-assembly routes and not from controlled synthesis [1].

Compared to rigid bridging ligands, flexible bridging tectons can produce some unique frameworks with beautiful and extraordinary aesthetics and useful properties because of their flexibility and conformational freedom [2–4]. However, owing to the difficulty in predicting the structures of the products, the rational design of coordination polymers from flexible ligands is still a formidable challenge [2].

Recently we have used the pseudopeptidic ligand terephthaloylbisglycine ($TBGH_2$) for the synthesis of networks with cds topology. Our synthetic strategy was to introduce flexibility on the aromatic rigid scaffold of terephthalic acid, in addition to groups that would allow extra stabilizing interactions and eventually to build up a higher dimensional motif through metal–ligand interactions. TBG^{2-} is longer than terephthalate, the carboxylate groups are reasonably free to rotate and the amide bond can be the source of hydrogen bonds that would be able to stabilize the network [3].

The next step in our research was to use open chain polycarboxylates, such as 1,2,3-propanetricarboxylic ($PTCH_3$) acid and 1,2,3,4-butanetetracarboxylic acid, which correspond, as far as the number of carboxylic groups is concerned, to trimesic and adamantanetetracarboxylic acid. Though there are no additional groups to provide extra stabilizing interactions, those carboxylic acids are very flexible, and bearing in mind that the smallest chelate ring could be formed upon coordination is seven membered, we anticipated metal-organic polymer formation. In presence

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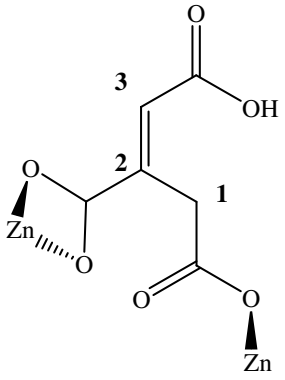
of Lewis bases such as 1,10-phenanthroline, 4,4′-bipyridine or 1,2-bis(4-pyridine)ethane, $PTCH^{2-}$ behaves as a μ_2-ligand and produces dimers or 2D polymers [4].

Trans-aconitic acid (LH_3) has been found to be a competitive inhibitor of aconitase in the Krebs cycle [5], and the mechanism of its action is still unclear. It has been found, in the solid state, that partially deprotonated *trans*-aconitate is rather flexible as hydrogen-bonded building block [6–8] or as a coordinated ligand [9,10]. Herein, we present the synthesis [11], the crystal structures [12] and the spectroscopic and thermal characterization [14] of two *trans*-aconitato bridged 1D coordination polymers $\{[Zn(HL)(phen)]_n \cdot n(H_2O)\}$ (**1**) and $\{[Zn(HL)(bpy)]_n \cdot 2n(H_2O)\}$ (**2**).

The crystal structures of both compounds consist of linear [Zn(LH)(N–N)] chains, running parallel to *b* axis and lattice water molecules held with H-bonds. (Fig. 1) Zinc atoms are bonded to two nitrogen atoms belonging to the chelated Lewis base and three oxygen atoms belonging to two different aconitate anions. Analysis of the shape-determining angles using the approach of Reedijk et al. [15] yields a value for trigonality index, τ, of 0.23 for **1** and 0.16 for **2** suggesting distorted square planar geometries about Zn in both compounds ($\tau = 0$ and 1 for perfect *sp* and *tbp* geometries respectively). The basal plane of each coordination polyhedron is defined by the two oxygen atoms belonging to a chelating carboxylate and the two nitrogen atoms belonging to phen (**1**) or bpy (**2**). The apical positions are occupied by the oxygen atom belonging to a unidentate carboxylate of a different *trans*-aconitate.

The three carboxylic groups in the ligand behave differently. (Scheme 1) The carboxylic group bonded on C1 is monodentate, the group on C2 is chelated, while the group on C3 remains protonated. The ligand bridges two Zn(II) ions leading to the formation of linear chains. To our knowledge, this coordination mode has not been observed previously for a tricarboxylic acid.

Bearing in mind the coordination of the ligand, the fluctuation of the the C–O bond lengths can be easily anticipated. For example, in polymer **1**, the shortest C–O



Scheme 1. Coordination mode of HL^{2-} ligand found in **1** and **2**.

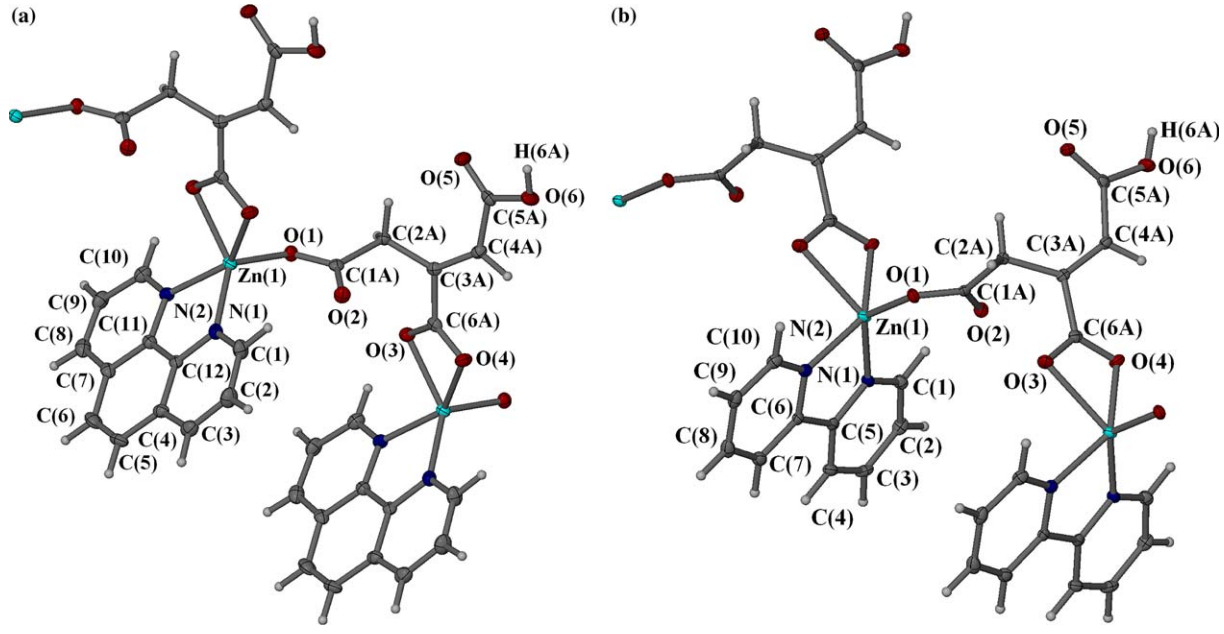


Fig. 1. Parts of the polymeric chains of **1**, (a) and **2** (b) drawn with 40% probability ellipsoids. Only non-hydrogen atoms of the asymmetric units are labeled for clarity. Selected bond lengths (Å) and angles (°): **1**: Zn(1)–O(1) 1.935(2), Zn(1)–N(1) 2.045(3), Zn(1)–N(2) 2.100(3), Zn(1)–O(3) 2.132(2), Zn(1)–O(4) 2.172(2), O(3)–Zn(1)–N(1) 123.54(11), O(3)–Zn(1)–N(2) 109.55(10), N(1)–Zn(1)–N(2) 80.43(11), O(1)–Zn(1)–O(3) 105.22(10), N(1)–Zn(1)–O(3) 130.34(10), N(2)–Zn(1)–O(3) 92.70(10), O(1)–Zn(1)–O(4) 101.26(10), N(1)–Zn(1)–O(4) 97.63(10), N(2)–Zn(1)–O(4) 144.21(10), O(3)–Zn(1)–O(4) 61.24(9); **2:** Zn(1)–O(1) 1.959(2), Zn(1)–N(1) 2.051(2), Zn(1)–N(2) 2.059(2), Zn(1)–O(4) 2.075(2), Zn(1)–O(3) 2.288(2), Zn(1)–C(6A) 2.512(3), O(1)–Zn(1)–N(1) 131.94(8), O(1)–Zn(1)–N(2) 105.99(8), N(1)–Zn(1)–N(2) 79.91(9), O(1)–Zn(1)–O(4) 100.28(7), N(1)–Zn(1)–O(4) 102.93(8), N(2)–Zn(1)–O(4) 141.34(8), O(1)–Zn(1)–O(3) 98.99(7), N(1)–Zn(1)–O(3) 129.06(8), N(2)–Zn(1)–O(3) 87.77(8), O(4)–Zn(1)–O(3) 60.15(7).

distances [C(5A)–O(5), 1.213(4); C(1A)–O(2), 1.225(4) Å] correspond to the terminal C–O's, the longest [C(1A)–O(1), 1.291(4); C(5A)–O(6), 1.332(4) Å] correspond to the monodentate carboxylate (O(1) is bonded to Zn(1)) and to the neutral carboxylic group (O(6) is bonded to H(6A)), while the C–O bond lengths of the chelated carboxylate have intermediate values [C(6A)–O(3), 1.267(4); C(6A)–O(4), 1.260(4) Å] suggesting delocalization of the negative charge.

In both compounds there are two different kinds of interactions that lead to the formation of 3D supramolecular architectures; hydrogen bonding and stacking interactions. In **1**, the lattice water molecule forms three hydrogen bonds (Table 1) and acts as a bridge between three different 1D chains. The first involves hydrogen atom H(21W) and a carboxylate oxygen from the chelated carboxylic group O(3), the second involves the other hydrogen atom of lattice water H(11W) and the coordinated carboxylate oxygen from the monodentate carboxylic group, O(1), of a different chain. Finally, the lattice water molecule acts as acceptor and forms the third hydrogen bond with the hydrogen atom of the free carboxyl, belonging to a third different chain resulting in the formation of thick layers (Fig. 2).

The 2D layers propagate parallel to the plane formed by *b* and the bisect of the *a*0*c* angle, and interact to each other through π–π stacking interactions between 1,10-phenanthroline moieties. The aromatic ligands utilize two adjacent rings for the stacking interaction, the central and one external. The distance between the least square planes is 3.471 Å, while the offset of the centroids of the central rings is 0.64 Å [16] (Figs. 3 and 4).

Table 1
Geometrical characteristics of H-bonds in **1**

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(6)–H(6A)···O(1W)#1	0.83	1.80	2.600(3)	162.4
O(1W)–H(11W)···O(1)#2	0.97	1.85	2.720(3)	148.7
O(1W)–H(21W)···O(3)	0.90	1.95	2.840(4)	173.0

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

The lattice of compound **2** contains two water molecules per asymmetric unit (Table 2). The first water molecule, O(1W), forms two intra-chain hydrogen bonds connecting the two coordinated carboxylates of the same ligand. The second lattice water molecule, O(2W), forms three hydrogen bonds, as in **1**, and acts as a bridge between three different 1D chains. The first involves hydrogen atom H(12W) and the coordinated oxygen from the monodentate carboxylic group O(1), the second involves the second hydrogen atom of lattice water H(22W) and a carboxylate oxygen from a chelate carboxylic group, O(3), of a second chain. O(2W) is also H-bonded to the hydrogen atom, of the free belonging to a third different strand, resulting in the formation of a thick layer having bpy moieties on the surface, as in **1**.

The 1D chains are arranged parallel in a way that bpy ligands of one chain are situated in the void spaces between the bpy ligands of a different layer. The bpy moieties of different layers are involved in π–π stacking, utilizing one ring [16]. The distance between the least square planes is 3.496 Å, with a centroid distance of 3.622 Å and an offset of 0.95 Å.

The IR spectra display broad bands centered at 3427 and 3447 cm^{-1} for **1** and **2**, respectively, in agreement with the presence of H-bonded water molecules. The multiple coordination of the ligand HL^{2-} makes the unambiguous assignment of the IR bands difficult; however some bands can be explained. The bands at 1714 cm^{-1} for **1** and 1713 cm^{-1} for **2** can be attributed to the *ν*(C=O) of the free carboxyl at position 3 (Scheme 1), while the pairs of bands at 1552 and 1425, and 1599 and 1423 cm^{-1} are characteristic for the symmetric and asymmetric COO stretching vibrations for **1** and **2**, respectively [17].

When the zinc polymer **2** is heated under nitrogen, an endothermic dehydration starts at 36 °C which is completed at 180 °C. The observed weight loss of 8.17% is in agreement with the calculated value of 8.38% for

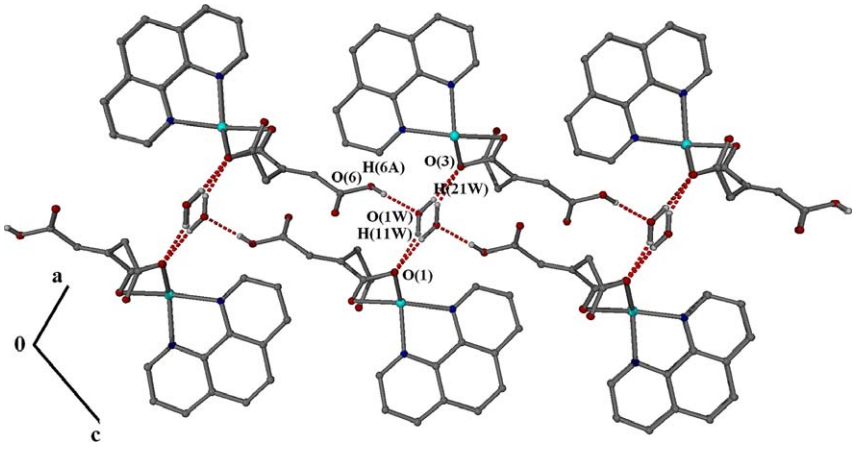


Fig. 2. A projection of the hydrogen bonded layer formed in **1**, parallel to *b*, showing the direction of the aromatic rings outside of the layer. The organic hydrogen atoms have been omitted for clarity.

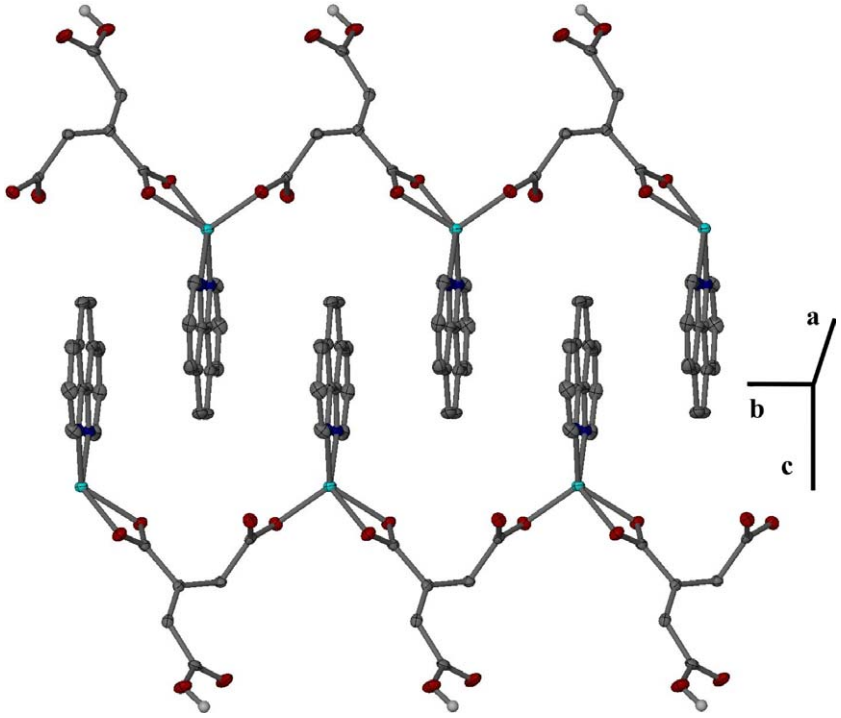


Fig. 3. The π–π stacking interactions between two different 1D chains.

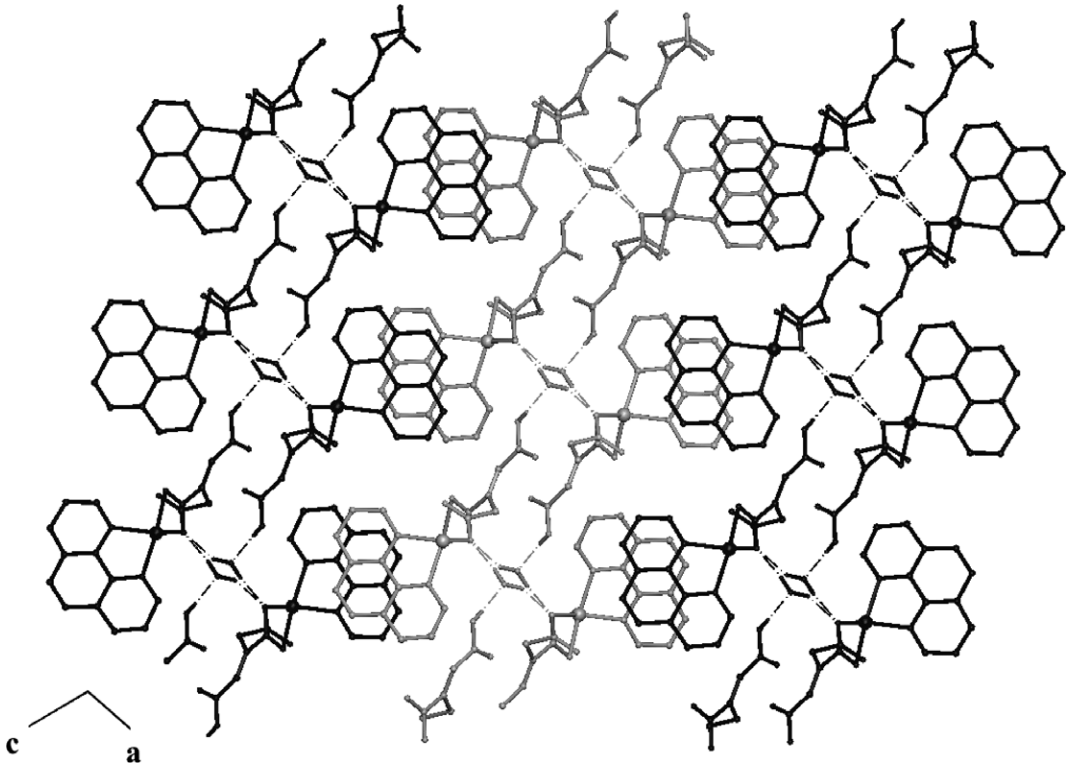


Fig. 4. A packing diagram of **1**, along the *b* axis. The hydrogen bonded layers are drawn in black and grey to emphasize the stacking interactions between the phen rings that lead to a 3D supramolecular architecture. Organic hydrogen atoms have been omitted for clarity.

two lattice water molecules. The anhydrous intermediate is stable up to 205 °C; at this point a rather complicated decomposition process begins, which involves at least three continuous steps as shown by the DTA curve. The decomposition proceeds up to 700 °C, where the white final residue corresponds to ZnO (found 19.1%, calculated 18.8%). Compound **1** afforded similar TG-DTA curves.

Table 2
Geometrical characteristics of H-bonds in **2**

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(6)–H(6A)···O(2W)#2	0.87	1.78	2.613(3)	158.7
O(2W)–H(12W)···O(1)	0.85	1.91	2.744(3)	167.6
O(2W)–H(22W)···O(3)#3	0.76	2.06	2.815(3)	170.7
O(1W)–H(11W)···O(4)	1.00	1.95	2.903(3)	158.5
O(1W)–H(22W)···O(3)#1	0.90	1.96	2.845(3)	168.7

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

In this work, we have synthesized and characterized two new linear coordination polymers using *trans*-aconitates as bridges. Surprisingly, the coordination mode of HL^{2-} differs from those have been reported previously [9,10]. Two additional kinds of interactions (i.e. H-bonding and π–π stacking) lead to the formation of 3D supramolecular architectures. Attempts to prepare and characterize coordination polymers with *trans*-aconitic acid and other open chain carboxylic acids are in progress.

Supplementary material

Crystallographic data for complexes **1** and **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 602872 and 602873. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or on the web http://www.ccdc.cam.ac.uk).

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References

[1] (a) O.M. Yaghi, H. Li, J. Am. Chem. Soc. 118 (1996) 295;
(b) O.M. Yaghi, H. Li, T.L. Groy, Inorg. Chem. 36 (1997) 4292;
(c) O.M. Yaghi, H. Li, T.L. Groy, J. Am. Chem. Soc. 118 (1996) 9096;
(d) J. Kim, B. Chen, T.M. Reineke, H. Li, M. Eddaoudi, D.B. Moler, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 123 (2001) 8239.
[2] P.J. Steel, Acc. Chem. Res. 38 (2005) 243.
[3] G.E. Kostakis, L. Casella, N. Hadjiliadis, E. Monzani, N. Kourkoumelis, J.C. Plakatouras, Chem. Commun. (2005) 3859.
[4] I. Vlahou, N. Kourkoumelis, A. Michaelidis, S. Skoulika, J. C. Plakatouras, Inorg. Chim. Acta, in press, doi:10.1016/j.ica.2006.03.001.
[5] J.F. Thomson, S.L.M. Nance, K.J. Bush, P.A. Szczepanik, Arch.Biochem. Biophys. 117 (1966) 65.
[6] J.M. Dargay, H.M. Berman, H.L. Carrell, J.P. Glusker, Acta Crystallogr. Sect. B 28 (1972) 1533.
[7] H.L. Carrell, Acta Crystallogr. B29 (1973) 2082.
[8] D. Braga, O. Benedi, L. Maini, F. Grepioni, J. Chem. Soc. Dalton Trans. (1999) 2611.
[9] M.-S. Wang, G.-C. Guo, M.-L. Fu, L. Xu, L.-Z. Cai, J.-S. Huang, Dalton Trans. (2005) 2899.
[10] M.-S. Wang, G.-C. Guo, L.-Z. Cai, W.-T. Chen, B. Liu, A-Q. Wu, J.-S. Huang, Dalton Trans. (2004) 2230.
[11] All reagents and solvents were of commercially available reagent quality unless otherwise stated. All the reactions were performed at room temperature and not special conditions were demanded. *Preparation of* $\{[Zn(HL)(phen)]_n \cdot n(H_2O)\}$ (**1**): $Zn(NO_3)_2 \cdot 3H_2O$ (39.2 mg, 0.15 mmol) was dissolved in H_2O (4 mL). To this, a solution of 1,10-phenanthroline (15 mg, 0.075 mmol) in hot H_2O (1 mL), was added. Separately, *trans*-aconitic acid, H_3L (17.4 mg, 0.1 mmol) was dissolved in water (5 mL) and was added to the metal solution. The resulting solution was left undisturbed for slow evaporation. The first crop of colorless crystals was isolated after 5 days; a second crop of crystals isolated after 2 weeks. Overall yield 80% (based on phen). Calc. for $C_{18}H_{14}N_2O_7Zn$, **1**: C, 49.62; H, 3.24. Found: C, 49.31; H, 3.19%. IR (KBr, cm^{-1}) = 3427 (s), 3073 (m), 2920 (w), 2554 (w), 1714 (s), 1623 (s), 1552 (s), 1521 (m), 1425 (s), 1364 (m), 1343 (m), 1241 (s), 1188 (s), 1108 (m), 933(w), 848 (s), 810 (m), 724 (s). *Preparation of* $\{[Zn(HL)(2,2'\text{-}bipy)]_n \cdot 2n(H_2O)\}$ (**2**): This complex was prepared by the procedure similar to that for **1** using bpy instead of phen. The formation of the crystals was slower and the last crop of crystals collected after almost 4 weeks. Overall yield: 72% (based on bpy). Calc. for $C_{16}H_{16}N_2O_8Zn$, **2**: C, 44.72; H, 3.75. Found: C, 44.23; H, 3.69%. IR (KBr) = 3447 (s), 3078 (m), 2994 (w), 2558 (w), 1713 (s), 1599 (s), 1423 (s), 1385 (m), 1340 (m), 1242 (s), 1192 (s), 1029 (w), 932 (w), 884 (w), 781 (m).
[12] Crystallographic data and structure refinement parameters: for $C_{18}H_{14}N_2O_7Zn$ (**1**): M_r = 435.68, monoclinic, $P2_1/n$, a = 14.3419(5), b = 7.1096(9), c = 17.2325(10) Å, β = 109.212(4)°, V = 1659.3(2) Å^3, Z = 4, D_c = 1.744 Mg m^{-3}, μ = 1.529 m m^{-1}, T = 120(2) K, 9969 reflections measured, 3231 unique ($R_{int.}$ = 0.0839). Parameters = 254, R_1(obs.) = 0.0406, wR_2(obs.) = 0.0894, R_1(all) = 0.0877, wR_2(all) = 0.1069. For $C_{16}H_{16}N_2O_8Zn$ (**2**): M_r = 429.68, monoclinic, $P21/n$, a = 15.3283(7), b = 7.0748(2), c = 16.1364(7) Å, β = 106.972(2)°, V = 1673.69(12) Å^3, Z = 4, D_c = 1.705 Mg m^{-3}, μ = 1.518 m m^{-1}, T = 120(2) K, 19.765 reflections measured, 2951 unique ($R_{int.}$ = 0.0801). Parameters = 244, R_1(obs.) = 0.0318, wR_2(obs.) = 0.0643, R_1(all) = 0.0572, wR_2(all) = 0.0734. X-ray diffraction intensities were collected at 120 K on a Nonius Kappa CCD diffractometer with ϕ and ω scans with κ offsets and Mo Kα radiation, l = 0.71073 Å. SHELX-97 was used for structure solution (SHELXS) and refinement (SHELXL) [13]. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically.
[13] SHELX97–Programs for Crystal Structure Analysis (Release 97-2). Sheldrick, G.M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
[14] The IR spectra were recorded on a Perkin–Elmer Spectrum GX FT-IR spectrophotometer using the KBr technique (range 4.000–370 cm^{-1}). The TG-DTA analysis was carried out under nitrogen, at a scan rate of 5 °C/min, on a Shimadzu DTG 60 apparatus. C, H and N analyses were conducted by the University of Ioannina, Greece, Microanalytical Service.
[15] A.W. Addison, T.N. Rao, J. Reedijk, J.V. Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
[16] (a) C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885;
(b) V. Russell, M. Scudder, I. Dance, J. Chem. Soc. Dalton Trans. (2001) 789.
[17] H. Carlsson, M. Haukka, E. Nordlander, Inorg. Chem. 43 (2004) 5681, and references therein.