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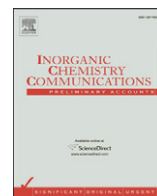


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# Synthesis, structural and theoretical studies of a rare hexameric water cluster held in the lattice of $\{[\text{Zn}(\text{HL})(\text{phen})(\text{H}_2\text{O})]\cdot 3(\text{H}_2\text{O})\}_2$ ( $\text{H}_3\text{L} = \text{trans}$ -aconitic acid)

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## ABSTRACT

The reaction of  $\text{Zn}(\text{NO}_3)_2 \cdot 3(\text{H}_2\text{O})$  with *trans*-aconitic acid ( $\text{H}_3\text{L}$ ), in presence of chelating 1,10-phenanthroline, leads to the formation of a dinuclear unit  $\{[\text{Zn}(\text{HL})(\text{phen})(\text{H}_2\text{O})]\cdot 3(\text{H}_2\text{O})\}_2$ . The lattice water molecules are assembled as a centrosymmetric hexamer. The crystal structure, thermal studies, theoretical calculations, and the factors that stabilize this water hexamer are presented.

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The crystal engineering of supramolecular metal–organic architectures assembled through coordination bonds as well as other weak cooperative interactions such as H-bonding,  $\pi$ – $\pi$  stacking and electrostatic interactions has developed rapidly and has attracted considerable interest in the design and construction of new crystalline materials. The design and synthesis of compounds with unique structure and function can be regarded as a long-term challenge. The motivation for this interest is the possibility to generate new materials with interesting architectures [1–4] and potential applications [5–8].

At the same time, theoretical studies have significantly contributed to the understanding of water structures and provided new structural features of water and new insights into the behavior of water with implications in biological and environmental contexts [9]. Small water clusters  $(\text{H}_2\text{O})_n$  ( $n = 4$ –10) are crucial building units for extended water morphologies including tapes [10] and layers [11] whose physical properties are closely associated with those of bulk water [12]. So far, a variety of tetramer [13], pentamer [14], hexamer [15], heptamer [16], octamer [17] and decamer [18] water clusters have been isolated in different solid crystalline hosts.

Our synthetic approach for the construction of coordination polymers or metal containing supramolecular architectures is based on the utilization of flexible bridging tectons along with 3d transition metal elements. So far, organic open chain polycarboxylates, such as 1,2,3-propanetricarboxylic (PTCH<sub>3</sub>) acid [19], *trans*-aconitic acid [20,21] and 1,2,3,4-butanetetracarboxylic acid, [19] have been

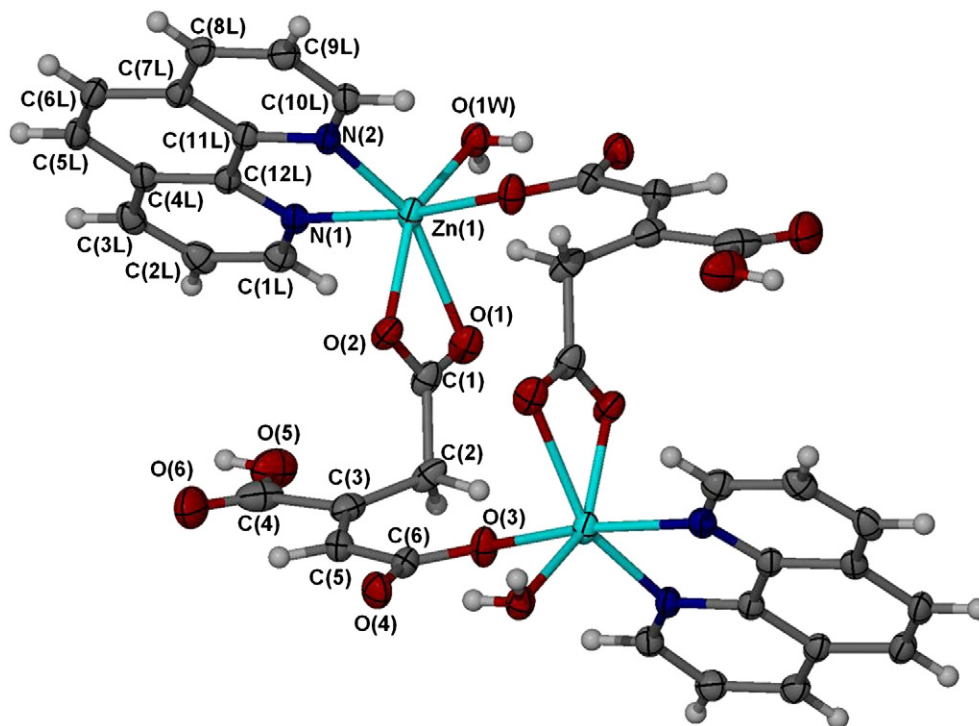
successfully incorporated in the construction of coordination polymers and multidimensional supramolecular networks. On the other hand, it is well known that the metal salt, the metal–ligand ratio, temperature, solvent and the time of reaction affect the nature of the final product. Bearing this in mind, and the fact that a 1D polymer was isolated without addition of any base [20], the next step in our systematic investigation on the Zn/*trans*-aconitate/1,10-phen system was to increase the pH of the solution and observe its influence on the structural diversity of the final products.

The reaction of  $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  with 1,10-phenanthroline and *trans*-aconitic acid (0.15/0.075/0.1 mmol ratio) in  $\text{H}_2\text{O}$  (10 mL) in the presence of  $\text{Na}_2\text{CO}_3$  (0.1 mmol) resulted after 2 weeks in the deposition of colorless crystals of a compound formulated as  $[\text{Zn}(\text{HL})(\text{phen})(\text{H}_2\text{O})]\cdot 3(\text{H}_2\text{O})$  (**1**) (Overall yield 80% based on phen). [22].

A perspective view of the dinuclear unit in **1** is shown in Fig. 1. Compound **1** crystallizes in the triclinic space group  $P\bar{1}$ , consisting of neutral dimeric units that are held together through hydrogen bonding and stacking interactions, while three lattice water molecules are located in the asymmetric unit [23]. The coordination number of each Zn(II) center is six, forming a distorted octahedron. Each zinc atom is bonded to two nitrogen atoms belonging to a chelated Lewis base, to three oxygen atoms belonging to two different aconitate anions and to an oxygen atom of a water molecule  $[\text{ZnN}_2\text{O}_4]$ . Compared to our previous work on the system Zn/*trans*-aconitate/1,10-phen system, the increase in pH results in a different geometry for the metal center, i.e. octahedral instead of square pyramidal [20]. The three carboxylic acid groups of the ligand behave in a different way in **1**. The central carboxylic acid group remains protonated while

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**Fig. 1.** The dimeric unit of **1**. Selected bond lengths (Å) and angles (°): Zn(1)—O(3)#1 2.053(2), Zn(1)—N(2) 2.080(3), Zn(1)—O(1 W) 2.090(3), Zn(1)—O(2) 2.095(3), Zn(1)—N(1) 2.152(3), Zn(1)—O(1) 2.389(3), O(3)#1—Zn(1)—N(2) 92.25(11), O(3)#1—Zn(1)—O(1 W) 89.02(11), N(2)—Zn(1)—O(1 W) 111.95(11), O(3)#1—Zn(1)—O(2) 89.54(10), N(2)—Zn(1)—O(2) 98.26(10), O(1 W)—Zn(1)—O(2) 149.80(10), O(3)#1—Zn(1)—N(1) 171.00(11), N(2)—Zn(1)—N(1) 78.85(11), O(1 W)—Zn(1)—N(1) 93.02(11), O(2)—Zn(1)—N(1) 93.07(10), O(3)#1—Zn(1)—O(1) 95.30(10), N(2)—Zn(1)—O(1) 154.98(10), O(1 W)—Zn(1)—O(1) 92.03(10), O(2)—Zn(1)—O(1) 58.08(9), N(1)—Zn(1)—O(1) 93.39(10). Symmetry transformation: #1  $-x, -y, -z + 2$ .

one of the rest is chelated and the other monodentate. This coordination mode of the carboxylate ligand has been observed previously in the similar reaction system Cd/*trans*-aconitate/Lewis base, which resulted in the formation of 1D  $[\text{Cd}(\text{HL})(\text{N}-\text{N})]$  linear chains with the geometry around the Cd(II) centers being octahedral  $[\text{CdN}_2\text{O}_4]$  [21]. In contrast, in compound **1** a dinuclear  $\{[\text{Zn}(\text{HL})(\text{phen})(\text{H}_2\text{O})]\cdot 3(\text{H}_2\text{O})\}_2$  unit is formed. (Fig. 1)

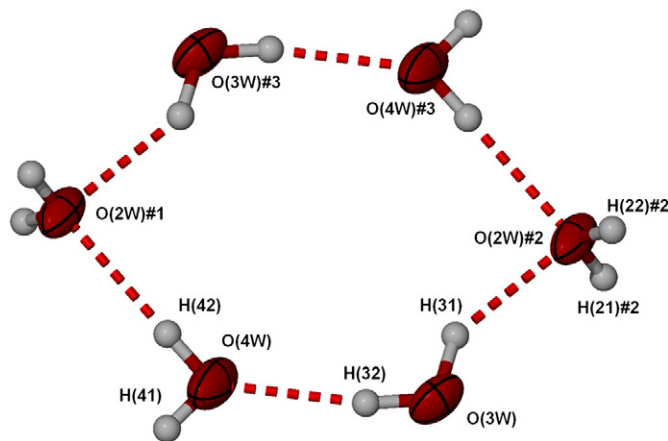
Bearing in mind the coordination of the ligand, the C—O bond lengths fluctuate; the shortest C—O distances  $[\text{C}(4)—\text{O}(6), 1.178(6)$ ;  $\text{C}(6)—\text{O}(4), 1.251(5)$  Å] correspond to the terminal CO's, the longest  $[\text{C}(6)—\text{O}(3), 1.271(5)$ ;  $\text{C}(4)—\text{O}(5), 1.301(6)$  Å] correspond to the monodentate carboxylate (O(3) is bonded to Zn(1)) and to the neutral carboxylic acid group (O(5) is bonded to H(6A)), while the C—O bond lengths of the chelated carboxylate have intermediate values  $[\text{C}(1)—\text{O}(1), 1.262(4)$ ;  $\text{C}(1)—\text{O}(2), 1.254(5)$  Å] suggesting delocalization of the negative charge.

The presence of three lattice and one terminal  $\text{H}_2\text{O}$  molecules, the uncoordinated and the protonated and deprotonated hydroxyl O atoms of the carboxylate ligand implies the existence of several hydrogen bonds around each dimeric  $\{[\text{Zn}(\text{HL})(\text{phen})(\text{H}_2\text{O})]\cdot 3(\text{H}_2\text{O})\}_2$  unit.

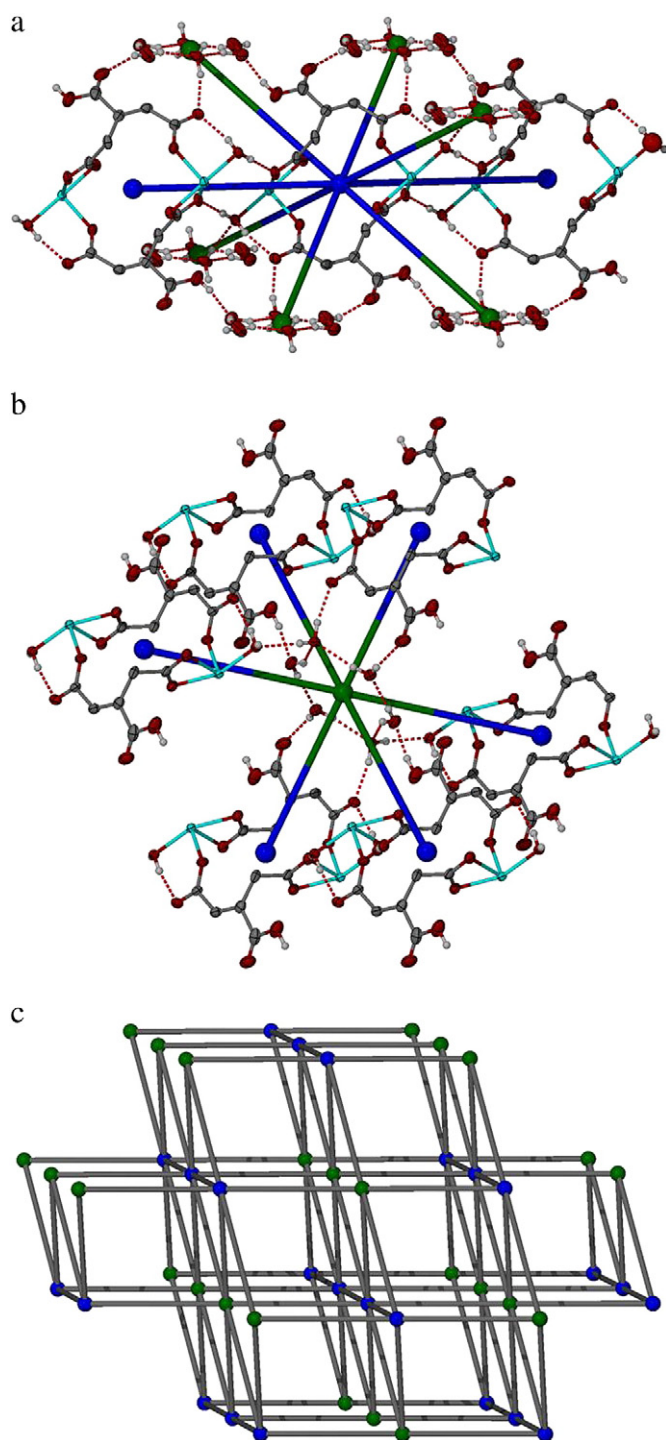
Interestingly, the three lattice water molecules O(2 W), O(3 W), O(4 W), and their symmetry related equivalents, form a cyclic water hexamer (Fig. 2). The  $\text{O}\cdots\text{O}\cdots\text{O}$  angles are in the range  $100.16$ – $134.67^\circ$ , while the six  $\text{O}\cdots\text{O}\cdots\text{O}\cdots\text{O}\cdots\text{O}$  torsional angles in the ring are  $-11.4$ ,  $-9.5$ ,  $-8.2$ ,  $8.2$ ,  $9.5$  and  $11.4^\circ$ . The hexamer thus approximates to a planar hexagon. The  $\text{O}\cdots\text{O}$  distance within the hexamer ranges from  $2.720(5)$  to  $2.801(5)$  Å with an average value of  $2.748(5)$  Å at 120 K, which may be compared with the  $\text{O}\cdots\text{O}$  distance in ice with icosahedral symmetry ( $2.759$  Å at 200 K) [25]. Two zinc-coordinated water molecules (O(1 W), cf. Fig. 1) are attached at two diagonally opposite ends of the hexagon at a distance of  $2.835(4)$  Å.

Moreover, the  $\{[\text{Zn}(\text{HL})(\text{phen})(\text{H}_2\text{O})]\cdot 3(\text{H}_2\text{O})\}_2$  dimeric units are linked by the adjacent planar water hexamers to form a 3D supramo-

lecular architecture (Fig. 3). Various  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding and stacking interactions can be identified (Table 1). The first involves the water clusters and the  $\{[\text{Zn}(\text{HL})(\text{phen})(\text{H}_2\text{O})]\cdot 3(\text{H}_2\text{O})\}_2$  dimeric units, while the second involves the aryl rings of the dimeric units, which both further stabilize the overall 3D metal-supramolecular framework of **1**. Each dinuclear unit links six hexameric water clusters through the two uncoordinated, O(4) and O(6), the protonated hydroxyl O(5) atom and the coordinated water molecule. Additionally each dinuclear unit is linked to two adjacent dinuclear units through the coordinated water molecule O(7), resulting in an 8-connected node. Thus, the decorated H-bonded framework of complex **1** can be represented as a binodal (6,8)-net with vertex symbol  $(3^2.4^{10}.5^2.6)$  for the 6-connected node and  $(3^4.4^{12}.5^8.6^4)$  for the 8-connected node. A search in the TOPOS database concludes that the topology of the H-bonded framework is unique.



**Fig. 2.** The planar water hexamer present in the lattice of **1**. Symmetry transformations to generate equivalent atoms: #1  $-x, -y, -z + 2$ , #2  $-x + 1, -y, -z + 2$ , #3  $x + 1, y + 1, z$ .



**Fig. 3.** Views of decorated units (a) 8-connected node, (b) 6-connected node (phen molecules have been omitted for clarity), and (c) the binodal (6,8) topological net produced.

The IR spectra display a broad band centered at  $3447\text{ cm}^{-1}$  in agreement with the presence of H-bonded water molecules. The multiple coordination of the ligand  $\text{HL}^{2-}$  makes the unambiguous assignment of the IR bands difficult; however some bands can be explained. The band at  $1713\text{ cm}^{-1}$  can be certified as the  $\nu(\text{C}=\text{O})$  of the free carboxylic group, while the pairs of bands at  $1563$  and  $1425\text{ cm}^{-1}$ , are characteristic for the symmetric and asymmetric COO stretching vibrations [26].

The thermogravimetric analysis shows that all water molecules can be removed in one step that begins at  $35^\circ\text{C}$  and ends at  $180^\circ\text{C}$

**Table 1**  
Hydrogen bonding and stacking interactions in 1.

D—H...A	d(D—H)	d(H...A)	d(D...A)	<(DHA)
O(1 W)—H(11)...O(1)#2	0.90(6)	1.75(6)	2.651(4)	178(5)
O(1 W)—H(12)...O(4)#1	0.78(5)	1.85(5)	2.616(4)	166(5)
O(2 W)—H(21)...O(1 W)	0.74(5)	2.10(6)	2.835(4)	176(5)
O(2 W)—H(22)...O(4)#3	0.88(6)	1.89(6)	2.750(4)	166(5)
O(3 W)—H(32)...O(4 W)	0.87(6)	1.89(6)	2.724(5)	162(7)
O(3 W)—H(31)...O(2 W)#4	0.90(4)	1.93(6)	2.720(6)	146(7)
O(4 W)—H(41)...O(6)#5	0.81(4)	2.05(4)	2.815(6)	158(4)
O(4 W)—H(42)...O(2 W)#6	0.81(6)	2.01(6)	2.801(5)	165(5)
O(5)—H(6A)...O(3 W)	0.86(4)	1.77(4)	2.623(5)	172(7)
Centroids	Centroids distance (Å)	Least square planes distance (Å)	Offset (Å)	
a...c#6	3.550(2)	3.360	1.146	
b...c#7	3.695(2)	3.334	1.593	

Symmetry transformations: #1  $-x, -y, -z + 2$ , #2  $-x + 1, -y, -z + 2$ , #3  $x + 1, y + 1, z$ , #4  $x, y - 1, z$ , #5  $-x, -y - 1, -z + 1$ , #6  $-x + 1, -y, -z + 1$ , #7  $-x, -y, -z + 1$ .

<sup>a</sup> N(1)—C(1 L)—C(2 L)—C(3 L)—C(4 L)—C(12 L), <sup>b</sup> N(2)—C(11 L)—C(7 L)—C(8 L)—C(9 L)—C(10 L), <sup>c</sup> C(4 L)—C(5 L)—C(6 L)—C(7 L)—C(11 L)—C(12 L).

(calculated for four water molecules 14.72%, found 14.67%). The dehydrated product is stable up to  $203^\circ\text{C}$ . Upon temperature increase, the dehydrated compound begins to decompose in two discrete steps. The final residue corresponds to the predicted ZnO (theoretical 16.60%, experimental 17.10%). Reversible solvent uptake is a common property. On heating the crystals of compound 1 at  $60^\circ\text{C}$  in vacuum for 120 min, the dehydrated product has an amorphous phase, indicating a collapse of the initial structure.

To gain some insight into the relative stabilities of the embedded planar centrosymmetric hexameric water clusters vis-à-vis other stable forms of the hexamer and its stepwise decomposition to isolated water molecules we performed DFT calculations [27] at the B3LYP/6-311++G(2d,2p) level. Water clusters including dimers, trimers, tetramers and larger oligomers have been well characterized by modern theoretical and experimental methods [9]. It is important to notice that cyclic hexameric water clusters constitute the structural motive in the  $I_h$  structure of ice [9,17]. The computed structure of the embedded cyclic planar centrosymmetric water hexamer along with the equilibrium geometries of  $(\text{H}_2\text{O})_n$  ( $n=1-6$ ) are visualized in Fig. 4. The harmonic vibrational analysis of the hexamer, confined in the cavity, showed that this structure corresponds to a saddle point of the 18th order (number of imaginary frequencies = 18) in line with previous theoretical studies [17].

The planar structure of the cyclic water hexamer confined in the cavities was found to be a structure of high energy, being unstable by 246.5 and 249.4 kcal/mol with respect to the “chair” and “boat” equilibrium geometries of cyclic water hexamers computed at the B3LYP/6-311++G(2d,2p) level. The “chair” conformation of the cyclic  $(\text{H}_2\text{O})_6$  clusters is slightly more stable than the “boat” conformation by 2.9 kcal/mol in excellent agreement with previous theoretical studies [28–32]. Therefore, it can be concluded that the planar cyclic centrosymmetric structure of the water hexamers confined in the cavities is stabilized by the restrained influence exercised by the cavities through additional hydrogen bonds.

Next we exploited the stepwise decomposition of the cyclic hexamer in order to throw light on the mechanism of formation of the cluster. The stepwise formation of the water hexamers from water molecules has extensively been investigated using experimental techniques, such as cluster growth in liquid helium [9] or hydrogen cyanide [33]. It was found that the water hexamers are formed by the stepwise insertion of water molecules in smaller cyclic water clusters. Perusal of Fig. 4 reveals that the stepwise insertion of water molecules to the cyclic trimer to form the tetramer and pentamer are the most



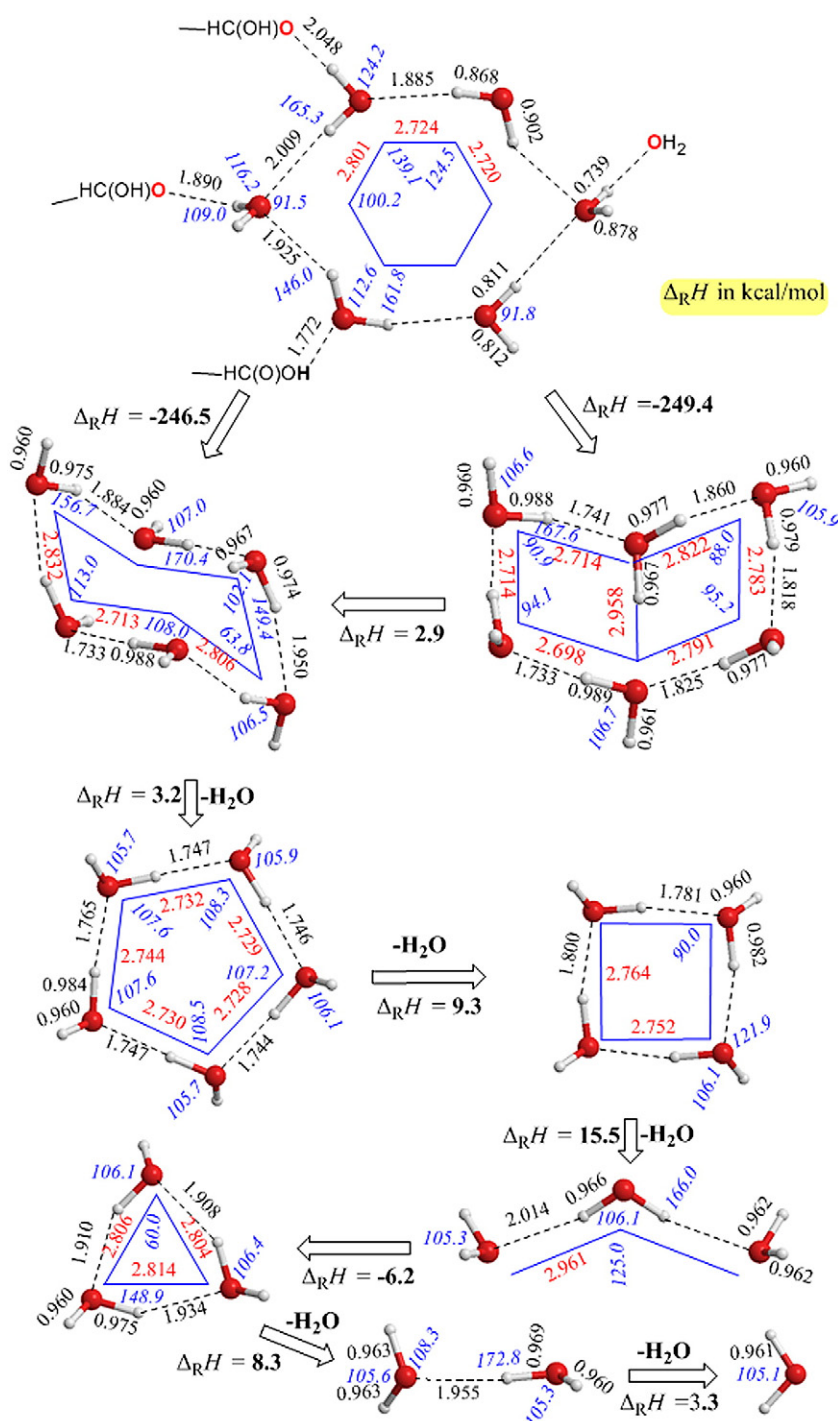


Fig. 4. Geometric and energetic profiles of  $(\text{H}_2\text{O})_n$  ( $n=1-6$ ) clusters computed at the B3LYP/6-311++G(2d,2p) level.

exoergic (exothermic) steps, while the final step of the addition of the water molecule to the pentamer to form the hexamer is almost thermoneutral ( $-3.2$  kcal/mol).

In this work, we have described a centrosymmetric planar water hexamer in the lattice of  $[\text{Zn}(\text{HL})(\text{phen})(\text{H}_2\text{O})] \cdot 3(\text{H}_2\text{O})$  (**1**). In comparison with our previous results, a slight increase of the pH value of the reaction system  $\text{Zn}(\text{NO}_3)_2 \cdot 3(\text{H}_2\text{O})/\text{trans}$ -aconitic acid/1,10-phenanthroline results in a different product. The lattice water assembles as a centrosymmetric hexamer. The present findings provide new structural data for the coordination mode of *trans*-aconitic acid.

## Acknowledgements

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## Appendix A. Supplementary material

CCDC 777266 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from the Cambridge

Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Supplementary data to this article can be found online at [doi:10.1016/j.inoche.2010.09.038](https://doi.org/10.1016/j.inoche.2010.09.038).

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- [21] G.E. Kostakis, G. Malandrinou, E. Nordlander, M. Haukka, J.C. Plakatouras, Polyhedron 28 (2009) 3227.
- [22] 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  $[\{Zn(HL)(phen)(H_2O)\}_3(H_2O)]_2$  (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. To the resulting solution  $Na_2CO_3$  (106 mg, 0.1 mmol) was added and then 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  $C_{18}H_{20}N_2O_{10}Zn$ , 1: C, 44.26; H, 4.13; N, 5.73. Found: C, 44.06; H, 4.03; N, 5.60%. IR (KBr,  $cm^{-1}$ ) = 3447 (s), 3073 (m), 2920 (w), 2554 (w), 1713 (s), 1623 (s), 1563 (s), 1521 (m), 1425 (s), 1364 (m), 1343 (m), 1243 (s), 1188 (s), 1108 (m), 933 (w), 848 (s), 810 (m), 724 (s). The IR spectra were recorded on a Perkin–Elmer Spectrum GX FTIR spectrophotometer with the samples as KBr pellets (range 4000–370  $cm^{-1}$ ). The TG–DTA analysis was carried out under nitrogen, at a scan rate of 5 °C/min, on a Shimadzu DTG 60 apparatus. The weight of the sample was about 8 mg. C, H and N analyses were conducted by the University of Ioannina, Greece, Microanalytical Service.
- [23] Crystallographic data and structure refinement parameters: for  $C_{18}H_{20}N_2O_{10}Zn$  (1): Mr = 489.73, triclinic,  $P\bar{1}$ ,  $a = 9.4346(4)$ ,  $b = 9.7944(6)$ ,  $c = 10.7849(7)$  Å,  $\alpha = 91.919(3)^\circ$ ,  $\beta = 98.971(4)^\circ$ ,  $\gamma = 94.679(4)^\circ$ ,  $V = 980.04(10)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.660$  Mg m<sup>-3</sup>,  $\mu = 1.315$  mm<sup>-1</sup>,  $T = 120(2)$  K, 14070 reflections measured, 4055 unique (Rint = 0.0401). Parameters = 318,  $R_1(obs.) = 0.0509$ ,  $wR_2(obs.) = 0.1192$ ,  $R_1(all) = 0.0635$ ,  $wR_2(all) = 0.1280$ . X-ray diffraction intensities were collected at 120 K on a Nonius Kappa CCD diffractometer with  $\varphi$  and  $\omega$  scans with  $\kappa$  offsets and Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å. SHELX-97 was used for structure solution (SHELXS) and refinement (SHELXL) [24]. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically.
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