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Oxozinc carboxylates: a predesigned platform for modelling prototypical Zn-MOFs' reactivity toward water and donor solvents†

Wojciech Bury,^{*a} Iwona Justyniak,^b Daniel Prochowicz,^a Zbigniew Wróbel^b and Janusz Lewiński^{*ab}

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Two unique adducts of an oxozinc carboxylate cluster with H₂O and THF were isolated and structurally characterized, [Zn₄(μ₄-O)(O₂CR)₆(H₂O)(THF)]·2(THF) and [Zn₄(μ₄-O)(O₂CR')₆(THF)₃] (where R = benzoate and R' = 9-antracenecarboxylate anion). The study shows that the zinc centers of the Zn₄O core can easily form unique coordination environments without breaking of the Zn–O_{carboxylate} bonds.

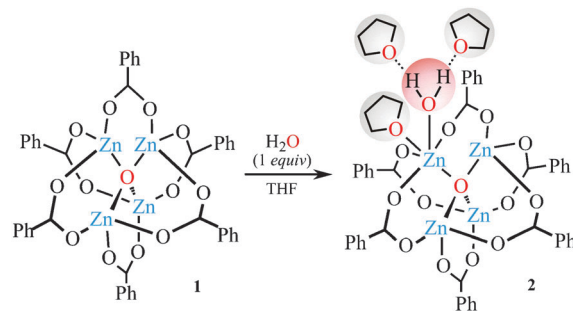
Oxozinc carboxylates are attracting a special attention as basic building units of a large class of prototypical microporous materials based on the tetranuclear cluster motif Zn₄O(O₂C[−])₆ linked by aromatic rings (designated further as Zn-MOFs).¹ Tremendous application potential of this type of materials in different fields has raised fundamental questions about the character of potential host–guest interactions involved in various processes. However, there is essentially a lack of experimental data on the character of interactions between the prototypical Zn₄O core and O-donor ligands so far,² and only very recent thermodynamic analysis of MOF-5 formation suggested that the solvent molecules may be space-filling rather than energetically important.³ Moreover, for a large number of MOFs that have been examined as heterogeneous catalysts, the intrinsic catalytic activity is connected with the Lewis acidity of the metal connecting points,⁴ however Zn₄O nodes were not considered as potential Lewis acidic sites.⁵

The effect of moisture on the stability of Zn-MOFs is another important and extensively explored issue.⁶ The disruptive effect of water on MOF structures was mentioned by Yaghi *et al.* in their early reports on the synthesis of prototypical MOFs^{6b} and this observation was examined experimentally in more detail by others.^{6d,6e,7} A recent molecular dynamics simulation on the MOF-5/H₂O system suggested that the coordination of H₂O molecules to the Zn₄O core leads to cleavage of one

Zn–O_{carboxylate} bond initiating the water-induced disruption mechanism.^{6c,8} In regard to the above-mentioned issues, research on fundamental transformations of oxozinc carboxylate clusters is highly desirable. Herein, we report on a top-down relationship involving oxozinc carboxylates as the predesigned molecular platform for modelling the reactivity of prototypical Zn-MOFs towards H₂O and tetrahydrofuran (THF).

In the course of our studies on the role of the carboxylate ligand in the oxygenation of alkylzinc complexes we have isolated the oxozinc carboxylate cluster [Zn₄(μ₄-O)(O₂CPh)₆] (**1**) in a moderate yield,⁹ which exhibits geometry parameters very similar to that observed in MOF-5¹⁰ (Table S1, ESI†). More recently encouraged by our recent results on the hydrolysis of zinc alkyls,¹¹ we developed a new efficient method for the preparation of oxozinc carboxylate clusters.¹² Having the prototypical oxozinc carboxylate clusters in hand we attempted to investigate their behaviour in the presence of moisture. In the equimolar reaction involving **1** and water, we successfully isolated from the post-reaction mixture colourless crystals of a unique cluster of the formula [Zn₄(μ₄-O)(O₂CPh)₆(H₂O)(THF)]·2(THF) (**2**) in high yield (Scheme 1).

Based on ¹H NMR as well as IR data for the post-reaction mixture of **1** with water we concluded that this reaction is shifted toward the product side (Fig. S5 and S6, ESI†). Compound **2** crystallizes in the monoclinic *P2₁/c* space group.† The structural analysis of **2** revealed the presence of an oxo-centred tetranuclear unit resembling that observed in compound **1**, however, in **2** the coordination sphere of the Zn1 centre is additionally completed by one H₂O and one THF molecule; as a result three Zn centres retain a tetrahedral environment and



Scheme 1

^a Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland.

E-mail: lewin@ch.pw.edu.pl, wojbur@ch.pw.edu.pl;

Web: <http://lewin.ch.pw.edu.pl>; Fax: (+) 48-22-234-7279

^b Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

† Electronic supplementary information (ESI) available: Experimental procedures and details of the structural solutions and X-ray data for **2** and **3**. CCDC 830650–830651. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc33094f

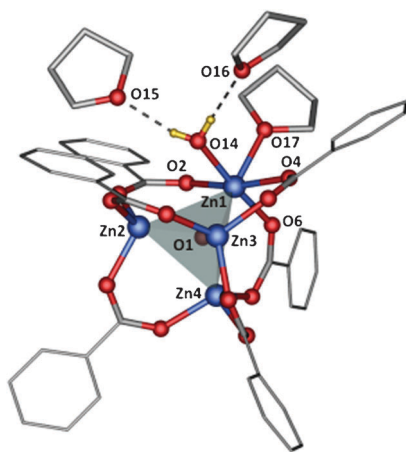
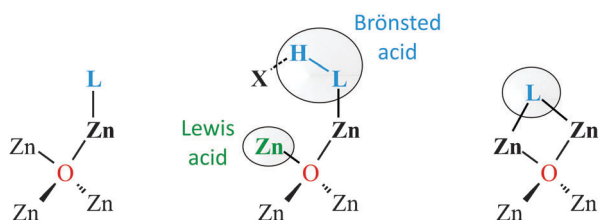


Fig. 1 Molecular structure of **2**; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1–O1, 2.027(4); Zn1–O2, 2.118(4); Zn1–O6, 2.067(4); Zn1–O14, 2.102(5); Zn1–O17, 2.183(4); Zn2–O1, 1.925(5); Zn3–O1, 1.932(4); Zn4–O1, 1.921(4); Zn1–O1–Zn2, 109.1(2); O17–Zn1–O14, 88.07(19); Zn2–O1–Zn4, 109.9(2).

the fourth one adopts a distorted octahedral coordination geometry (the Zn1–O14 and Zn1–O17 distances are 2.102(5) Å and 2.183(4) Å, respectively) (Fig. 1). The zinc oxo-cluster is additionally solvated by two THF molecules which are linked to the coordinated water molecule by intermolecular hydrogen bonds (the O14···O15 and O14···O16 distances are equal 2.727(2) Å and 2.669(7) Å, respectively) forming the second coordination shell. Interestingly, as shown on a structure overlay (Fig. S3, ESI[†]), the tetrahedral geometry of the Zn₄O core in **2** is closely related to that in **1**, and only a minor elongation of the Zn1–O1 bond can be noticed (2.027(4) Å vs. 1.950(6) Å, respectively). A more pronounced effect of the coordinated H₂O and THF molecules to the Zn1 atom concerns the Zn1–O_{carboxylate} bond lengths which are moderately longer than the corresponding distances in **1** and MOF-5, with the average elongation of *ca.* 0.15 Å (Table S1, ESI[†]). Moreover, the planes of the aromatic rings belonging to only two of the carboxylate ligands are noticeably shifted in comparison to the situation observed in **1**, while in the case of the four remaining benzene rings this structural effect is essentially smaller. The isolation of stable cluster **2** provides direct structural evidence for the initial interaction of H₂O with the prototypical Zn₄O core and undoubtedly demonstrates that the coordinated water molecule can be regarded as a molecular germ by attracting and binding other donor molecules with the formation of the second coordination sphere in Zn-MOFs and acting as a Brønsted acid assisted Lewis acid system (Scheme 2).



Scheme 2 Possible coordination modes of the oxozinc core with aprotic and protic donor ligands.

When a more bulky carboxylate ligand, namely 9,10-antracenedicarboxylic acid (Adc-H₂) was employed as a building block in the construction of an ultramicroporous PCN-13 network by Zhou *et al.*, distortion of the basic oxozinc node with subsequent increasing of the coordination number on three of the four zinc atoms was observed.^{8b} Interestingly, in the structure of this Zn-MOF there was no significant change of the coordination modes of carboxylate ligands implying that this type of binding mode is energetically favourable for carboxylate ligands. To have a more indepth understanding of the role of a steric hindrance of the carboxylate ligand on the geometry of oxozinc core we have chosen 9-antracene-carboxylic acid (Ant-H) as a monofunctional analogue of Adc-H₂. By applying a synthetic procedure involving 3 equiv. of Ant-H and 2 equiv. of Et₂Zn in THF followed by the addition of 0.5 equiv. of water yielded a novel oxozinc cluster solvated by three THF molecules, [Zn₄(μ₄-O)(O₂CAnt)₆(μ₁-O_{THF})₂(μ₂-O_{THF})] (**3**). Thus, the Et₂Zn/Ant-H/H₂O system afforded unexpectedly a direct picture of the interaction of a donor solvent with a prototypical Zn-MOF. Compound **3** crystallizes in a *P*1 space group and its molecular structure consists of a discrete, monomeric oxo-centered tetranuclear unit with six μ-1,2-carboxylate bridges and three THF molecules coordinated to two Zn atoms (Fig. 2).[†] Strikingly, two THF molecules act as monodentate ligands and the third one involves two electron lone pairs of the oxygen atom in the formation of a μ₂-O bridge between two zinc centres forming a non-planar four-membered Zn₂O₂ ring. Thus, to our knowledge it is the first instance that the prototypical Zn₄O core of Zn-MOFs is simultaneously able to coordinate a donor ligand in monodentate and bidentate fashion (Scheme 2). The Zn–O distances involving the bridging THF (Zn1–O15 2.427(7) Å and Zn2–O15 2.588(8) Å) are longer than those observed for mono-coordinated THF molecules (Zn1–O14 2.160(7) Å and Zn2–O16 2.137(8) Å). As is shown in Fig. 2, Zn1 and Zn2 atoms are six-coordinate, whereas Zn3 and Zn4 retain their tetrahedral coordination environment. The Zn–O_{oxo} bond lengths in **3** are very similar to those observed in **1** and MOF-5. In contrast, the Zn–O_{carboxylate} bonds involving

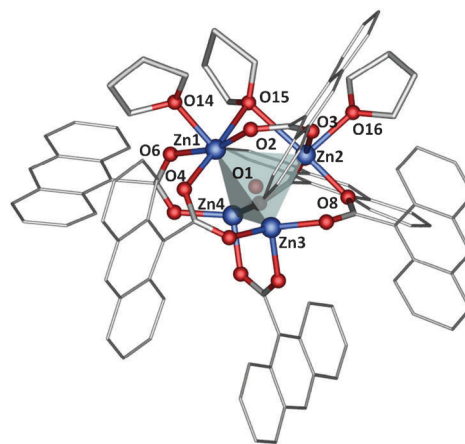


Fig. 2 Molecular structure of **3**; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1–O1, 1.999(6); Zn1–O2, 2.028(6); Zn1–O6, 2.075(6); Zn1–O14, 2.160(7); Zn1–O15, 2.427(7); Zn2–O1, 1.986(6); Zn2–O15, 2.588(8); Zn2–O16, 2.137(8); Zn3–O1, 1.917(6); Zn4–O1, 1.923(5); Zn1–O1–Zn2, 108.3(3); Zn1–O15–Zn2, 80.1(2).

the Zn1 and Zn2 atoms are slightly longer (with the average elongation of *ca.* 0.1 Å) than the corresponding distances in **1** and MOF-5 due to the coordination of THF molecules (for a more detailed comparison of the geometrical parameters of the compounds in question see Table S1, ESI†). Thus, the results demonstrate that the prototypical oxozinc cluster is able to accommodate additional donor ligands *via* the Lewis acid–base interaction without substantial changes in its central core.

Surprisingly, our results supported by a survey on the Cambridge Structural Database showed that oxozinc carboxylate species with five-coordinated zinc centres are very rare (*cf.* the structure of PCN-13),^{8b} thus in the discussed systems the tetrahedral and octahedral coordination environment for zinc atoms seems to be favoured. Importantly, the presence of coordinated donor molecules in the reported complexes does not lead to breaking (dissociation) of Zn–O_{carboxylate} bonds, however a slight spatial displacement of carboxylate ligands, in comparison to the Zn₄O(O₂CPh)₆ model cluster, can be observed.¹³ It is therefore reasonable to expect that the basic prototypical Zn-MOF's core can initially present similar coordinating abilities towards water and other donor molecules. These observations can also be a starting point in the discussion on the catalytic activity of Zn₄O-type complexes, as well as in the construction of more reliable molecular models for computational studies on MOF systems, which can be a valuable extension of the previously proposed theoretical model in which octahedral geometry around a Zn centre was not taken into account.

In conclusion, we demonstrated that the basic prototypical Zn₄O core can coordinate H₂O or other donor molecules with changing coordination geometry around zinc centres but preserving the oxozinc core essentially unchanged. Such fundamental studies are vital for a better understanding of how water can affect the prototypical MOF structure and the revealed propensity of oxozinc nodes towards the formation of covalent as well as non-covalent coordination spheres indicates that Zn-MOF nodes are prone to act as cooperative catalysts.

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Notes and references

† Crystal data for **2**: C₅₄H₅₆O₁₇Zn₄; *M* = 1238.55, crystal dimensions 0.42 × 0.30 × 0.20 mm³, monoclinic, space group *P*2₁/*c* (no. 14), *a* = 23.1389(9) Å, *b* = 11.6701(5) Å, *c* = 24.0951(5) Å, β = 117.427(2)°, *U* = 5775.1(4) Å³, *Z* = 4, *F*(000) = 2544, *D*_c = 1.424 g m^{−3}, *T* = 100(2) K, μ(Mo–Kα) = 1.707 mm^{−1}, θ_{max} = 21.97°, *R*₁ = 0.0541, *wR*₂ = 0.1051 for 5152 reflections with *I*_o > 2σ(*I*_o). CCDC – 830651.

Crystal data for **3**: C₁₀₂H₇₈O₁₆Zn₄; *M* = 1820.12, crystal dimensions 0.42 × 0.30 × 0.20 mm³, triclinic, space group *P*1̄ (no. 2), *a* = 14.302(3) Å, *b* = 14.733(3) Å, *c* = 23.048(5) Å, α = 103.534(14)°, β = 98.096(8)°, γ = 105.510(16)°, *U* = 4441.1(18) Å³, *Z* = 2, *F*(000) = 1874, *D*_c = 1.361 g m^{−3},

T = 100(2) K, μ(Mo–Kα) = 1.134 mm^{−1}, θ_{max} = 21.97°, *R*₁ = 0.0678, *wR*₂ = 0.1631 for 6197 reflections with *I*_o > 2σ(*I*_o). CCDC – 830650.

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- Presented results support the formation of complexes **2** and **3**, however they do not rule out other possibilities such as leaching of complex in solution preceded by metal–oxygen bond breaking.