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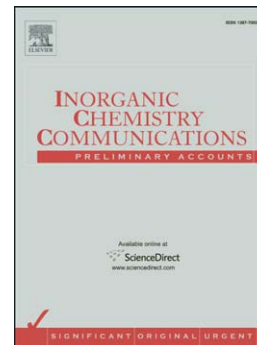
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# Novel hexanuclear and octanuclear zinc alkyl cages derived from a bis-oxamidate ligand

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**ABSTRACT:** **1** and **2** were prepared by coordination self-assembly from reacting *N,N'*-bis(3,5-di-*tert*-butyl-2-phenol)oxamide (L-H<sub>4</sub>) with ZnEt<sub>2</sub> in toluene and THF, respectively. The molecular X-ray structures show **1** as an octanuclear Zn<sub>8</sub> cage and **2** as a hexanuclear Zn<sub>6</sub> cage. The nuclearity of these cages is driven by the solvent, in fact **1** gives **2** upon addition of THF. Good polymer conversions for the ROP of *rac*-lactide were achieved by using **1** and **2** with alcohols as co-catalysts.

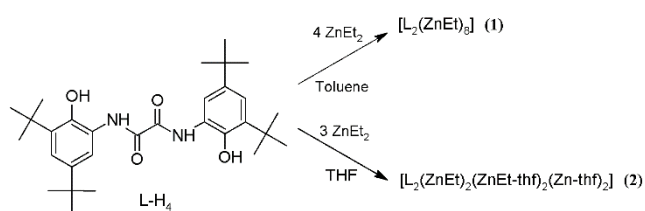
Nanosopic supramolecular 3D metallic cages obtained by coordinative self-assembly of polydentate ligands and metallic centers have been associated to polyhedrons with high punctual symmetry such as Archimedean and Platonic solids. The synthesis of these cages relies on the preorganization imposed by the first coordination sphere of the metallic center and the ligand-metal bond lability that allows self-correction during the cage formation. Thus, several strategies (directional bonding, symmetry interaction, molecular paneling, weak link, and bimetallic building block) have been envisioned to the so called rational design of supramolecular metallic cages.<sup>1</sup> On the other hand, there are a plethora of self-assembled nanoscopic metallic cages obtained by accident or without a “rational design” principle. Wimpenny defined this approach as “serendipitous self-assembly”.<sup>2</sup> Within this approach, ligands with complicated synthesis schemes must be avoided, small variations on the ligands should be explored and a range of crystallization solvents are mandatory to be examined. Accordingly, self-assembled 3D metallic cages obtained rationally or by serendipity have received considerable attention due to their aesthetic molecular architectures, host to guest properties, magnetic and electronic functions and their diverse applications such as photochemical and magnetic devices, in catalysis for organic reactions, multimetalloceptors, enzyme mimics, and in multinuclear cooperative catalysis.<sup>3</sup> The polynuclear nature of these species demands a better understanding of factors that control nuclearity such as modification of reaction conditions including type of counterion,<sup>4</sup> solvent,<sup>5</sup> pH,<sup>6</sup> ligand,<sup>7</sup> and even temperature.<sup>8</sup> Hence, the rational control of metallic complexes nuclearity remains challenging for coordination chemists. In this sense, carboxylate,<sup>9</sup> pyrazolate,<sup>10</sup> phosphonate<sup>11</sup> and polydentate ligands have been used to obtain polynuclear complexes.<sup>12</sup> Among those, zinc complexes have gained interest because they are appropriate enzymes models,<sup>13</sup> and active catalysts in the following: copolymerization of cyclohexene oxide and CO<sub>2</sub>;<sup>14</sup> conversion of esters, lactones, and carboxylic acids to oxazolines;<sup>15</sup> chemoselective acylation of alcohols;<sup>16</sup> deprotection of acetates and benzoates;<sup>17</sup> cycloaddition of CO<sub>2</sub> to epoxides;<sup>18</sup> transesterification;<sup>19</sup> and cyclic carbonate synthesis.<sup>20</sup> Bis-nucleating Salen ligands containing N<sub>2</sub>O<sub>2</sub> coordination sites plus additional nO<sub>2</sub> atoms introduced in the ligand backbone are excellent scaffolds to construct zinc cages.<sup>4a, 18</sup> Salen and Salamo bis-nucleating ligands produce

heptanuclear Zn<sub>7</sub> cages, which are moderate catalysts in the cycloaddition of CO<sub>2</sub> to epoxides.<sup>18</sup> These species are metallamacrocycles with capped-truncated-cones shape containing a tetrahedral [Zn<sub>4</sub>O]<sup>6+</sup> aggregate.<sup>13a</sup> The Zn<sub>3</sub> metallamacrocycle is able to accommodate other ions such as La<sup>3+</sup>.<sup>21</sup> It has been shown that there is a template effect of the trinuclear metallamacrocycle that allows the stepwise addition of Zn<sup>2+</sup> ions in the 3O<sub>2</sub> sites, i.e. the progression Zn<sub>3</sub>→Zn<sub>4</sub>→Zn<sub>5</sub>→Zn<sub>6</sub>→Zn<sub>7</sub> might be envisioned. In this context the Zn<sub>4</sub> and Zn<sub>6</sub> species were isolated and characterized.<sup>4a, 22</sup> In particular, nuclearity of Zn<sub>6</sub> and Zn<sub>7</sub> metallamacrocycles seems to be controlled by the counter ion. It was shown that the use of a slightly bulkier EtCO<sub>2</sub><sup>-</sup> anion instead of MeCO<sub>2</sub><sup>-</sup>, lowers the nuclearity of Zn<sub>7</sub> species to give Zn<sub>6</sub> species.<sup>4a</sup>

Herein, we disclose the synthesis, spectroscopic characterization and single crystal X-ray diffraction studies of two zinc polynuclear complexes [L<sub>2</sub>(ZnEt)<sub>8</sub>] (**1**) and [L<sub>2</sub>(ZnEt)<sub>2</sub>(ZnEt-THF)<sub>2</sub>(Zn-THF)<sub>2</sub>] (**2**) derived from ZnEt<sub>2</sub> and proligand bis(3,5-di-*tert*-butyl-2-phenol)-oxamide, L-H<sub>4</sub>. Remarkably, nuclearity control is exercised by the absence or availability of THF to afford **1** or **2**, respectively. In addition, the catalytic activity of **1**, **2** in the ROP of *rac*-lactide was examined.

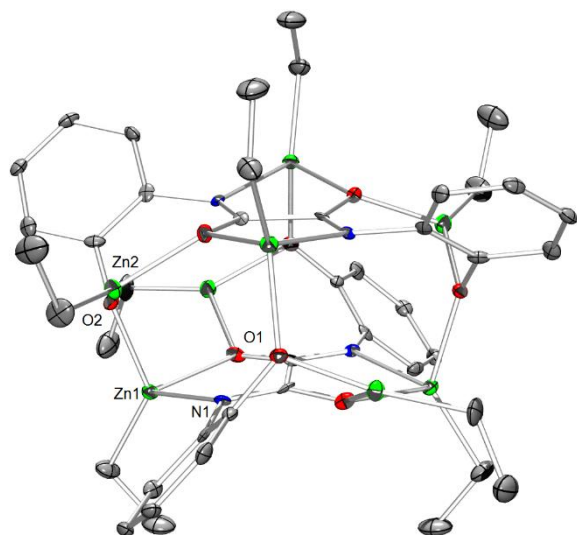
**1** was obtained as a yellow crystalline solid in 91% yield *via* alkane elimination by reacting ZnEt<sub>2</sub> and L-H<sub>4</sub><sup>23</sup> in a 4:1 stoichiometric ratio in toluene. When the reaction among ZnEt<sub>2</sub> and L-H<sub>4</sub> was carried out in a 3:1 stoichiometric ratio in presence of THF/toluene or neat THF, **2** was isolated as a yellow crystalline solid in 87% yield. Both complexes are air sensitive and **1** shows decomposition in CDCl<sub>3</sub> solution after few days (Scheme 1).

**Scheme 1. Synthesis of Zn<sub>8</sub> (cage 1) and Zn<sub>6</sub> (cage 2)**



Characterization of **1** and **2** was performed by spectroscopic methods, single crystal X-ray crystallography and elemental microanalysis.  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$  showed one domain of resonance signals for the aromatic protons and methyl substituents on the phenoxide rings, suggesting some degree of symmetry of the complex in solution (Figure S1). This is supported by the molecular X-ray structure, which displays  $S_4$  symmetry (Figure 1). As a consequence, two ZnEt moieties may be distinguished; one set shows signals at  $\delta$  1.14 ppm and 0.53 ppm assigned to four  $\text{O}_2\text{ZnEt}$  fragments, and other set shows signals at  $\delta$  0.65 ppm assigned to four  $\text{O}_2\text{NZnEt}$  fragments, and a diastereotopic methylene at  $\delta$  0.04 ppm and  $-0.12$  ppm. In contrast, the spectrum for **2** shows two domains of resonance signals for the aromatic protons and methyl substituents on the phenoxide rings, reflecting **2** has lower symmetry than **1** (Figure S3). Similarly to **1**, two sets of  $\text{ZnCH}_2\text{CH}_3$  moieties are distinguished, those ascribed to two  $\text{O}_3\text{ZnEt}$  fragments at  $\delta$  0.97 ppm and  $-0.06$  ppm and those assigned to two  $\text{O}_2(\text{THF})\text{ZnEt}$  fragments at  $\delta$  0.42 ppm and  $-0.06$  ppm. The resonance signals of one aromatic group are particularly shifted to  $\delta$  8.69 ppm due to an intramolecular  $\text{C}\cdots\text{O}=\text{C}$  interaction on the ligand, this is corroborated in the X-ray molecular structure discussed below (Figure 1). This interaction has also been observed in complexes derived from L- $\text{H}_4$  ligand and Sn(IV), Si(IV), Ge(IV).<sup>23-24</sup> The  $^{13}\text{C}$  NMR spectra of **1** and **2** are fully consistent with the  $^1\text{H}$  NMR data (Figure S2 and Figure S4). One set of carbon signals are observed for the aromatic and the *tert*-butyl groups for both compounds. As it was expected, the signals ascribed to four of each  $\text{O}_2\text{ZnEt}$  and  $\text{O}_2\text{NZnEt}$  fragments are observed at  $\delta$  12.24 ppm, 3.30 ppm; and 11.33 ppm, 0.48 ppm, respectively. In the case of **2**, two domains of signals ascribed to the ligand are clearly distinguished, and the signals from the  $\text{O}_3\text{ZnEt}$  and  $\text{O}_2(\text{THF})\text{ZnEt}$  fragments are observed at  $\delta$  11.83 ppm, 1.11 ppm; and 11.24 ppm,  $-1.17$  ppm.

**1** crystallizes in a tetragonal  $P4(2)/n$  space group and **2** in the orthorhombic  $Pnna$  space group (Figures 1 and 2). The molecular structure of **1** can be thought as one bis(oxamidate) ligand in a *trans*-conformation binding four Zn ions, then this moiety is related to a similar one by an improper  $S_4$  axis giving an octanuclear,  $\text{Zn}_8$ , 3D cage with overall  $S_4$  symmetry (Figure 1).

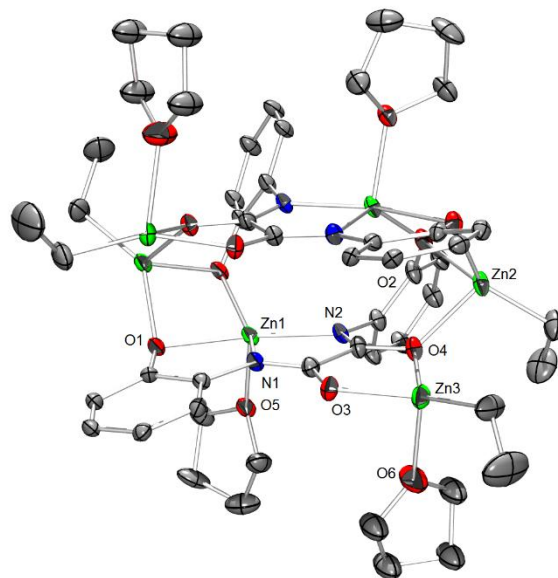


**Figure 1.** X-ray structure of  $\text{L}_2(\text{ZnEt})_8$  (**1**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and *t*Bu substituents have been omitted for clarity.

The two tetranuclear moieties are connected via four Zn-O bonds ( $\text{Zn1-O2}$  2.026(3) Å) using the perpendicular phenoxide

substituents to the  $\text{C}_2\text{N}_2\text{O}_2$  plane.  $\text{Zn}_8$  cage is assembled with four 9-membered  $\text{C}_2\text{NO}_3\text{Zn}_3$  rings in a boat conformation, four 7-membered  $\text{C}_3\text{NO}_2\text{Zn}$  rings also displaying a boat conformation, and four almost planar 5-membered  $\text{C}_2\text{NOZn}$  rings. The resultant polyhedron has 16 faces. The coordination geometry about Zn ions is distinguished into two domains with four ions each, the first domain features tri-coordinated Zn ions,  $\text{O}_2\text{ZnEt}$ , in a highly distorted trigonal environment ( $\text{O1-Zn2-C16}$  125.66(19)°,  $\text{O2-Zn2-C16}$  143.16(19)°,  $\text{O1-Zn-O2}$  91.17(13)°). For the second domain, the Zn ions are tetra-coordinated,  $\text{NO}_2\text{ZnEt}$ , in a highly distorted tetrahedral geometry ( $\text{C18-Zn1-O2}$  132.44(18),  $\text{N1-Zn1-O1}$  79.58(13)°). The Zn-C [1.941(5)-1.973(5) Å], Zn-N [2.092(4) Å], Zn-O [1.934(3)-2.093(3) Å] bond lengths are similar to those described for other polynuclear zinc complexes such as  $[\text{Na}_6\{\text{Zn}_6(\text{ccdp})_3(\mu_6\text{-SO}_4)\}(\text{OH})\cdot 10.5\text{H}_2\text{O}]$  (Zn-N 2.204(11)-2.237(12) Å and Zn-O 2.018(8)-2.249(10) Å)<sup>25</sup>,  $[(\text{Ls})_4\text{Zn}_8(\text{H}_2\text{O})_3]$  (Ls = 3-hydroxysalato, [Zn-N 2.010-2.187 Å, Zn-O 1.923(10)-2.115(14) Å]<sup>26</sup>,  $(\text{Lt})_2(\text{ZnEt})_6\cdot 3\text{C}_6\text{H}_6$ , Lt = tris(3,5-dimethyl-2-hydroxyphenyl)methane) [Zn-C 1.961(2) Å, Zn-O 1.985(2)-2.001(2) Å]<sup>14</sup>, and  $[(\text{Li})_4(\text{Zn})_4]$  (Li = N,N'-ethylenebis(4-iminopentan-2-one)), Zn-N 1.984(3)-1.996(3), Zn-O 1.936(3)-1.939(3) Å).<sup>27</sup>

The molecular structure of **2** shows a hexanuclear,  $\text{Zn}_6$ , 3D cage with overall  $\text{C}_2$  symmetry (Figure 2). In this case the structure can be thought as one bis(oxamidate) ligand in a *cis*-conformation binding three zinc ions. This moiety is related to a similar one by a proper  $\text{C}_2$  axis. Nuclearity control seems to be exercised in **1** and **2** by the absence or presence of the Lewis base THF, respectively. Our experiments showed that  $\text{Zn}_8$  easily affords  $\text{Zn}_6$  upon THF addition into a toluene solution of **1** with concomitant formation of  $\text{ZnEt}_2$  and ethane (Figure S5).



**Figure 2.** X-ray structure of  $[\text{L}_2(\text{ZnEt})_2(\text{ZnEt-THF})_2(\text{Zn-THF})_2]$  (**2**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and *t*Bu substituents have been omitted for clarity.

The two trinuclear moieties are connected via Zn-O bonds ( $\text{Zn2-O1}$  1.995(4),  $\text{Zn2-O4}$  2.119(4),  $\text{Zn2-O2}$  2.058(4) Å) using a perpendicular phenoxide and a carbonyl substituent from the ligand.  $\text{Zn}_6$  is assembled with one 10-membered  $\text{C}_4\text{N}_2\text{O}_2\text{Zn}_2$  ring in a boat conformation, two 7-membered  $\text{C}_3\text{N}_3\text{O}_2\text{Zn}$  rings also displaying a boat conformation, two almost planar 5-membered  $\text{C}_2\text{N}_2\text{Zn}$  rings, two almost planar 5-membered  $\text{C}_2\text{O}_2\text{Zn}$  rings, and two four planar 4-membered  $\text{O}_2\text{Zn}_2$  rings. In agreement with the

$^1\text{H}$  NMR data, an intramolecular  $\text{C}=\text{O}\cdots\text{H}$  interaction of 2.238 Å is observed, which is shorter than the sum of the van der Waals radii for hydrogen ( $r_{\text{VDW}} = 1.2$  Å) and oxygen ( $r_{\text{VDW}} = 1.50$  Å). **2** displays three coordination domains for zinc. In the first domain, two zinc ions show tetra-coordinated  $\text{O}_2(\text{THF})\text{ZnEt}$  fragments in a very distorted tetrahedral environment, where three O atoms two comes from the ligand carbonyls and the third comes from THF. A second domain shows two zinc ions in highly distorted tetrahedral  $\text{O}_2\text{ZnEt}$  fragments, but in this case two O atoms are provided by phenoxide substituents and one O comes from a carbonyl substituent. The third domain shows two penta-coordinated  $\text{ON}_2(\text{THF})\text{Zn}$  fragments in a distorted *tbp* coordination geometry ( $\chi = 0.58$ ); where two O atoms are provided by two phenoxides and one O by THF, the two N atoms come from the amide substituents. The Zn–C (1.940(7)–1.969(6) Å), Zn–N (1.990(4)–2.084(4) Å) and Zn–O (1.941(4)–2.215 Å) bond lengths are in the range of  $\text{Zn}_8$  species and other complexes, *vide supra*.

Two important factors can be identified on the process  $\text{Zn}_8 \rightarrow \text{Zn}_6$ : one factor is the increasing of coordination number of two zinc ions on addition of THF to **1** (tetrahedral to *tbp*), and the other factor is the isomerization of the bis-oxamate ligand from the *trans* to the *cis*-conformer. It is very well known that *cis*-conformation of bis-oxamides favors low nuclearity complexes due to the easy access of metallic centers to the four donor atoms ( $\text{N}_2\text{O}_2$ ) available on the ligand.<sup>28</sup>

Both complexes were moderately active for the ROP of *rac*-lactide, however good polymer conversions are achieved by using  $^i\text{PrOH}$  and  $\text{BnOH}$  with **1** and **2**. Polymerization experiments were carried out with a 100:1 monomer:initiator and results are given in Supporting Information Table S3. The low performance of **1** and **2** could be attributed to the low polarity of the Zn–C bond and the lipophilic nature of the cages. Spacefill X-ray models of **1** and **2** (Figure S6) show that in both complexes the  $^i\text{Bu}$  and  $\text{Et}$  substituents project outward the core of the aggregates precluding easy access of LA to the metallic centers, which in combination with long reaction times favor transesterification of PLA chains. An additional factor operating in the differences observed in  $M_{n,\text{calcd}}$  and  $M_{n,\text{exptl}}$  is the formation of lower nuclearity species, upon coordination of LA. To improve the performance of catalysts,  $^i\text{PrOH}$  and  $\text{BnOH}$  were used to obtain derivatives with polar Zn–OR bonds. The best results were obtained with  $\text{BnOH}$  (entries 3 and 8 in Table S3).

## ASSOCIATED CONTENT

### Supporting Information

Experimental details; NMR spectra of **1** and **2** and alkoxide derivatives; details of X-ray single crystal studies for **1** and **2** and CCDC reference numbers 1057248-1057249 (**2** and **1**, respectively). This material is available free of charge via the Internet at <http://dx.doi.org/10.1016/j.inoche>

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