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Shape-Persistent Octanuclear Zinc Salen Clusters: Synthesis, Characterization, and Catalysis

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S Supporting Information

ABSTRACT: We describe a selective and template-controlled synthesis of a series of Zn_8 metal complexes based on a bis-nucleating salen ligand scaffold. Our results, a combination of X-ray analysis and solution studies, show that discrete, shape-persistent metal clusters can be prepared in high yield. Their activity in organic carbonate catalysis is a function of the metal-connecting fragment present in the exterior of the cluster complex. The high stability of the clusters has been confirmed by ^1H, ^{13}C (DEPTQ) and DOSY NMR, gel permeation chromatography, high-performance liquid chromatography, and mass spectrometry.

The selective synthesis of defined cluster compounds remains an attractive challenge because these may offer materials with interesting photochemical and magnetic properties, and self-assembly features.[1] In this respect, Schiff base ligands such as salens have proven to be excellent directional ligands, in particular in those cases where additional O-donor atoms have been introduced in the backbone of the ligand scaffold.[2] Such systems are best designated as bis-nucleating because the usual central N_2O_2 coordination pocket is flanked by an outer shell of four O atoms, forming a O_4 cavity into which a wide variety of cations can be assembled.[3] Selective introduction of metal ions in the N_2O_2 and O_4 pockets can be achieved to furnish heterometallic complexes that can be of great use in (asymmetric) catalysis.[4] Shibasaki et al. have reported on such heterodinuclear Schiff base complexes that proved to be powerful catalysts in organic synthesis.[5] The metal ion in the outer "O_2-O_2" coordination shell may help to shape the coordination geometry around the metal ion in the N_2O_2 salen pocket, thereby offering a way to fine-tune important catalytic objectives such as enantio- and diastereoselectivity. Despite the effectiveness of such bimetallic derivatives in asymmetric catalysis, in most cases there is little information available on the structural features that are related with the actual catalysts, and higher-order cluster compounds have been proposed and observed mainly on the basis of mass spectrometric evidence.[6] Bermejo et al. reported on the formation of octanuclear Zn_8 clusters based on bis-nucleating salen scaffolds (for an example, see Figure 1, X = C).[7] In this case, flexible spacers between the salicylidene units were probed, although chiral diamines were not investigated in the assembly process. At a later stage, Nabeshima et al. utilized a structurally related salamo (or bis-oxime) type ligand (Figure 1, X = O), which resulted, upon metalation with zinc(II), in a similar Zn_8 cluster derivative.[8] Despite the fact that both types of cluster compounds were easily formed, the scope of these cluster complexes has been surprisingly limited to only a few examples and chiral analogues have thus far not been reported. Furthermore, catalytic application of these clustered complexes was neither intended nor proposed, which may have been a result of the observed fragmentation under mass spectral conditions. Here, we report on a series of new octanuclear Zn_8 cluster complexes that have been conveniently assembled in a single step from readily available precursors. Beside nonchiral diamines, we have also investigated the incorporation of various chiral diamines to give chiral cluster compounds. Their stability in solution has been studied in detail, and these investigations have shown these new cluster compounds to be shape-persistent and having molecular structures similar to those found in the solid state. Interestingly, the reactivity of these Zn_8 cluster compounds can be modified by the introduction of appropriate bridging groups, as illustrated by their application in CO_2 fixation catalysis.[9]

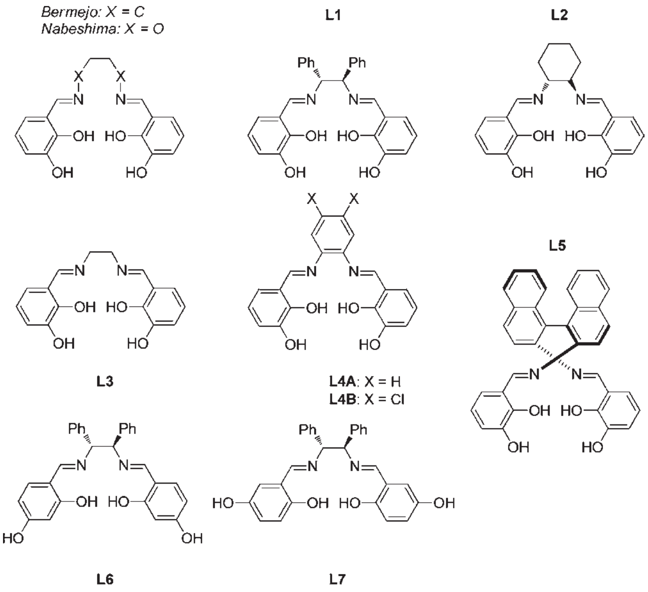

Figure 1. Bis-nucleating salen/salamo ligands used by Bermejo and Nabeshima and ligands (**L1**−**L7**) used in this work.

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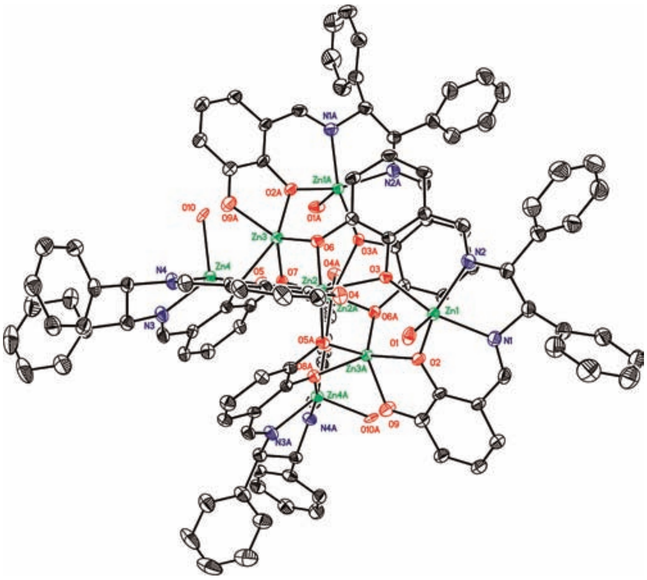


Figure 2. Crystal structure for $[\mathbf{L1}Zn_2]_4$ showing an octanuclear complex. Cocrystallized solvent molecules and H atoms are omitted for clarity, and only a partial labeling scheme is illustrated.

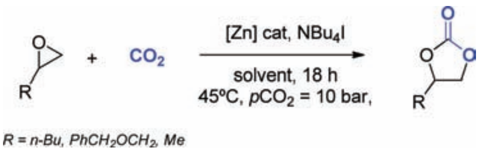
As a starting point for our studies, we chose chiral ligand **L1** and divalent zinc as the metal ion because it allows for various coordination geometries and previous results with comparable dinucleating ligands gave access to high-nuclear zinc cluster complexes.[7,8] While the coordination geometry inside the N_2O_2 salen pocket is relatively rigid, in the outer region of **L1**−**L5**, it is obvious that such a multidentate ligation mode is restricted and the assembly of multiple ions is required in this region. Upon combination of **L1** with 2 equiv of $Zn(OAc)_2 \cdot 2H_2O$ in refluxing ethanol and isolation of the precipitate (97% yield) upon cooling, a bright-yellow solid was obtained. This solid was analyzed by ^{1}H NMR [dimethylformamide (DMF)-d_7] and showed the presence of four diagnostic doublets for the bridgehead protons, indicating the presence of a higher-order species. The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum showed only one peak at m/z 2316.1 consistent with molecular formula $[\mathbf{L1}Zn_2]_4$, i.e., a tetrameric, octanuclear species (see the Supporting Information, SI). The presence of multiple zinc metal centers is particularly useful because they provide a true molecular signature (isotopic pattern) and allow for quick identification of higher-order, clustered materials. In order to get more insight in the solution structure, gel permeation chromatography (GPC; THF = tetrahydrofuran), high-performance liquid chromatography (HPLC; THF), and diffusion-ordered spectroscopy (DOSY; ^{1}H NMR) analyses (see the SI) were additionally performed. The GPC/HPLC trace showed only one peak in line with a single species under these polar conditions. The DOSY NMR was performed in both THF-d_8 and DMF-d_7, with both cases showing similar results; the molecular radius (R = 10.5 Å) was estimated using the Stokes−Einstein equation, which is significantly beyond the dimensions of the monomeric unit $\mathbf{L1}Zn_2$. Fortunately, crystals were obtained from acetone/CH_3CN, and the molecular structure is depicted in Figure 2.[10,11]

The molecular structure shows the assembly of four $\mathbf{L1}Zn_2$ units with the Zn ions in the N_2O_2 pockets having an axial H_2O ligand. Each of the "inner" Zn ions are surrounded by five O-atom donors, of which from each N_2O_4 salen unit three form μ_2-phenoxo bridges between two Zn ions. Interestingly, the space available for axial coordination of external ligands to the Zn ions ligated by the N_2O_2 sections of these binucleating systems seems to be limited because the interatomic distance from the coordinated H_2O ligand and the nearest O atom of an adjacent ligand is only ~2.5 Å. The molecular radius of tetrameric $\mathbf{L1}Zn_2$ (about 10−10.5 Å) corresponds well with that derived from the DOSY experiment, further supporting the presence of the octanuclear structure in solution.

Because only a few of these Zn_8 cluster compounds have been reported and the selective formation and stability have been the subject of some debate, we then investigated the influence of the flexibility of the diamine reagent on the outcome of the assembly process (**L1**−**L7** in Figure 1). Using a similar synthetic protocol and in those cases where ligands **L2**−**L4** were utilized, octanuclear cluster complexes could be conveniently isolated in moderate-to-good yields (Scheme S1). All compounds displayed a single peak in the mass spectra and single NMR resonance patterns (see the SI), indicating a high molecular stability. The X-ray structures for $[\mathbf{L4a}Zn_2]_4$ and $[\mathbf{L4b}Zn_2]_4$ were also solved (see the SI), and crystals were grown from DMF or DMF/MeOH; surprisingly, the exterior Zn ions located in the N_2O_2 coordination pockets are axially coordinated by H_2O (for $[\mathbf{L4a}Zn_2]_4$) or MeOH (for $[\mathbf{L4b}Zn_2]_4$), a result that points to steric infringement around these metal centers, preventing coordination of the larger DMF. When a rather flexible diamine precursor such as 1,8-diaminooctane was explored, an insoluble material resulted, which may be due to the formation of a polymeric structure rather than a discrete assembly, as observed with **L1**−**L4**. Also, in the case of **L5**, a dimeric rather than a tetrameric assembly was supported by mass spectrometry (see the SI). Whereas **L1** in the presence of excess $Zn(OAc)_2$ yields exclusively octanuclear complexes, in the case of **L6** and **L7** (Figure 1), the selective formation of monozinc complexes was observed (see the SI and Scheme 1; the complex based on **L7** was contaminated with an aldehyde reagent); this clearly demonstrates the requirement for close proximity of the O-atom donors to mediate the formation of larger discrete assemblies.

The results from the crystallographic analyses prompted us to investigate the catalytic reactivity of these clusters because the H_2O ligands should be fairly easy to displace by suitable substrates and thus act as Lewis acid activators. As a model reaction, we chose the cycloaddition reaction of carbon dioxide to terminal epoxides to afford cyclic carbonates,[9b] because recent literature has demonstrated that mononuclear Zn(salen)s are excellent catalyst systems for this transformation under relatively mild conditions.[10] As a benchmark substrate, we selected epoxyhexane, and NBu_4I was utilized as a cocatalyst at 45 °C and p_{CO_2} = 10 bar. The solubility of the octanuclear cluster complexes (except for $[\mathbf{L1}Zn_2]_4$) in CH_2Cl_2 and methyl ethyl ketone (MEK) was limited, and THF therefore had to be used instead to compare the cluster complexes in the catalytic studies (Table 1, entries 1−5). Only in the case of $[\mathbf{L1}Zn_2]_4$ was a significant amount of the cyclic carbonate observed (21% yield, entry 5), whereas the use of all of the other Zn_8 clusters showed virtually no product formation (1−3%). This contrasts our previous results with various mononuclear Zn(salen) catalysts in this reaction because in these studies the salphen [salphen = N,N-bis(salicylidene)imine-1,2-diaminobenzene] systems were clearly the most active mediators in cyclic carbonate synthesis. However, these salphen systems also show a higher affinity for axial binding of O-donor ligands, which may effectively compete with substrate binding. Therefore, it seems that the overall

Table 1. **Catalytic Performance of the Cluster Compounds in the Cycloaddition of CO_2 to Epoxides**[a]



entry	catalyst	solvent	yield[b]
1	(**L2**Zn$_2$)$_4$	THF	3
2	(**L3**Zn$_2$)$_4$	THF	1
3	(**L4a**Zn$_2$)$_4$	THF	1
4	(**L4b**Zn$_2$)$_4$	THF	1
5	(**L1**Zn$_2$)$_4$	THF	21
6	**L6**Zn	THF	41
7	(**L4b**Zn$_2$)$_4$	DCM[c]	1
8	(**L1**Zn$_2$)$_4$	DCM	2
9	(**L4b**Zn$_2$)$_4$	MEK[c]	22
10	(**L1**Zn$_2$)$_4$	MEK	35
11[d]	(**L1**Zn$_2$)$_4$	MEK	43
12[e]	(**L1**Zn$_2$)$_4$	MEK	87

[a] Reactions carried out with epoxyhexane as the substrate (unless stated otherwise) at 45 °C, p_{CO_2} = 10 bar, 2.5 mol % catalyst (i.e., reactive Zn ions) and 2.5 mol % cocatalyst (NBu_4I), and reaction time = 18 h. [b] Yield of carbonate product determined by ^1H NMR (DMSO-d_6) using mesitylene as the internal standard. [c] The catalyst was only partially soluble. [d] The substrate was benzyl glycidyl ether. [e] The substrate was propylene oxide; reaction time = 68 h.

reactivity of the outer Zn ions is determined by the axial substrate binding ability, steric factors, and flexibility of the bridging fragment in the salen ligand. Compared with the mononuclear systems **L6**Zn (entry 6, 41% yield), the complex [**L1**Zn$_2$]$_4$ shows a reduced overall activity.

A higher yield of carbonate product was achieved in MEK, amounting to 35% in the case of [**L1**Zn$_2$]$_4$ and 22% with [**L4b**Zn$_2$]$_4$ (entries 9 and 10) despite the fact that the latter catalyst is only partially soluble. Then we examined some other substrates in the cycloaddition reaction using catalyst system [**L1**Zn$_2$]$_4$. The benzyl glycidyl ether was converted to its corresponding carbonate in 43% yield (entry 11) under similar conditions, while propylene carbonate was obtained in high yield (87%, entry 12) after a 68 h reaction time.

In summary, we have presented a new series of (chiral) octanuclear Zn_8 cluster complexes based on readily available dinucleating ligands **L1**−**L4** and the first example of a catalytic application of these multinuclear systems. The analytical data support that these octanuclear systems are stable in solution and retain a shape-persistent, spherical structure. The outer-positioned Zn ions are axially coordinated by a H_2O ligand, which can be displaced by epoxidic substrates. These clusters were tested as catalysts for the cycloaddition of carbon dioxide to these oxiranes to give cyclic carbonates: the nature of the bridging fragment gives a tool to optimize the reactivity of these cluster derivatives in catalysis with [**L1**Zn$_2$]$_4$, surprisingly being the most active in this series. A current focus is the use of these metal cluster materials in other types of catalysis, while taking advantage of their nanoscale dimensions useful in separation from product and/or substrate flows.[11]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Full details on the synthesis and characterization of all new compounds and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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