

# Synthesis, catalytical activity and crystal

## structure of $[\text{Zn}_7(\mu^4\text{-O})_2(\mu^2\text{-O}_2\text{CH}_3)_{10}(4\text{-}^t\text{bupy})_2]$

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### 1. Introduction

Tetranuclear clusters  $[\text{M}_4(\mu^2\text{-O}_2\text{CR})_6\text{O}]$  ( $\text{M} = \text{Zn}$ ,  $\text{R} = \text{CF}_3$ ,  $\text{CH}_3$  and  $\text{M} = \text{Co}$ ,  $\text{R} = \text{CF}_3$ ) are effective catalysts for transesterification, alkoxyacylation of anilines and the synthesis of cyclic carbonates [1-3]. In these examples amines or ammonium salts are used as reagents or cocatalysts. The activation of a metal cluster using an amine should lead to a more active species than the unmodified cluster. In the case of 4-Dimethylaminopyridin (DMAP) Mashima et al proposed dinuclear species “ $\text{Zn}_2\text{-(dmap)}_m$ ” or trinuclear species “ $\text{Zn}_3\text{-(dmap)}_m$ ”, or their equilibrium mixture, generated from tetranuclear zinc cluster as catalytically active species [1]. Our interest is focused on the investigation of catalytically active species formed in reaction of the acetate cluster  $[\text{Zn}_4(\mu^4\text{-O})(\text{O}_2\text{CCH}_3)_6]$  in the presence of an aromatic amine.

In this note we report the structural characterization of  $[\text{Zn}_7\text{O}_2(\text{O}_2\text{CCH}_3)_{10}(^t\text{bupy})_2]$  ( $^t\text{bupy} = 4\text{-tertiary-Butylpyridine}$ ) formed in a catalytical reaction of  $[\text{Zn}_4(\mu^4\text{-O})(\text{O}_2\text{CCH}_3)_6]$  in presence of  $^t\text{bupy}$ .

### 2. Results and discussion

## 2.1 $[Zn_4(\mu^4-O)(O_2CCH_3)_6]$ and $[Zn_7O_2(O_2CCH_3)_{10}(^t\text{bupy})_2]$ as catalysts in transesterification and polymerisation

As described for  $[Zn_4(\mu^4-O)(O_2CCF_3)_6]$  [1] also  $[Zn_4(\mu^4-O)(O_2CCH_3)_6]$  is an active catalyst in the transesterification reaction. A yield of 88% could be achieved in the transesterification reaction of methyl benzoate with n-decanol in toluene. Under these reaction conditions no cocatalytical effect using <sup>t</sup>butylpyridine could be observed. In contrast addition of an equimolar amount of <sup>t</sup>bupy in relation to the used zinc catalyst leads to a lower yield in transesterification reaction of 65%. We found that this is the result of the formation of  $[Zn_7O_2(O_2CCH_3)_{10}(^t\text{bupy})_2]$  together with the precipitation of  $Zn(O_2CCH_3)_2$ . The use of ten times higher amount of <sup>t</sup>bupy leads to a yield of transesterification of 80%. This is the same value with could be achieved using only <sup>t</sup>bupy without the presence of any zinc compound [4] (table 1). NMR-Experiments in dichloromethane-d<sub>2</sub> showed a slight activity in ring opening polymerization of lactide using  $[Zn_7O_2(O_2CCH_3)_{10}(^t\text{bupy})_2]$  as catalyst. We observed its ability to convert 200 equivalents of lactide in 10 days at room temperature. The tetrameric Zinc cluster  $[Zn_4(\mu^4-O)(O_2CCH_3)_6]$  in comparison showed no catalytical activity in the polymerization of lactide at all. As well <sup>t</sup>bupy shows no activity.

**Table 1**

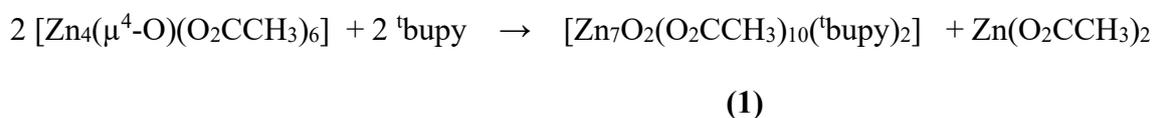
results of transesterification experiments

catalyst	<sup>t</sup> bupy	yield
$[Zn_4(\mu^4-O)(O_2CCH_3)_6]$	-	88%
$[Zn_4(\mu^4-O)(O_2CCH_3)_6]$	1	65%
$[Zn_4(\mu^4-O)(O_2CCH_3)_6]$	10	80%

(5 mol% catalyst, mol equivalent <sup>t</sup>bupy )

## 2.2 Preparation of $[Zn_7O_2(O_2CCH_3)_{10}(^t\text{bupy})_2]$ (**1**)

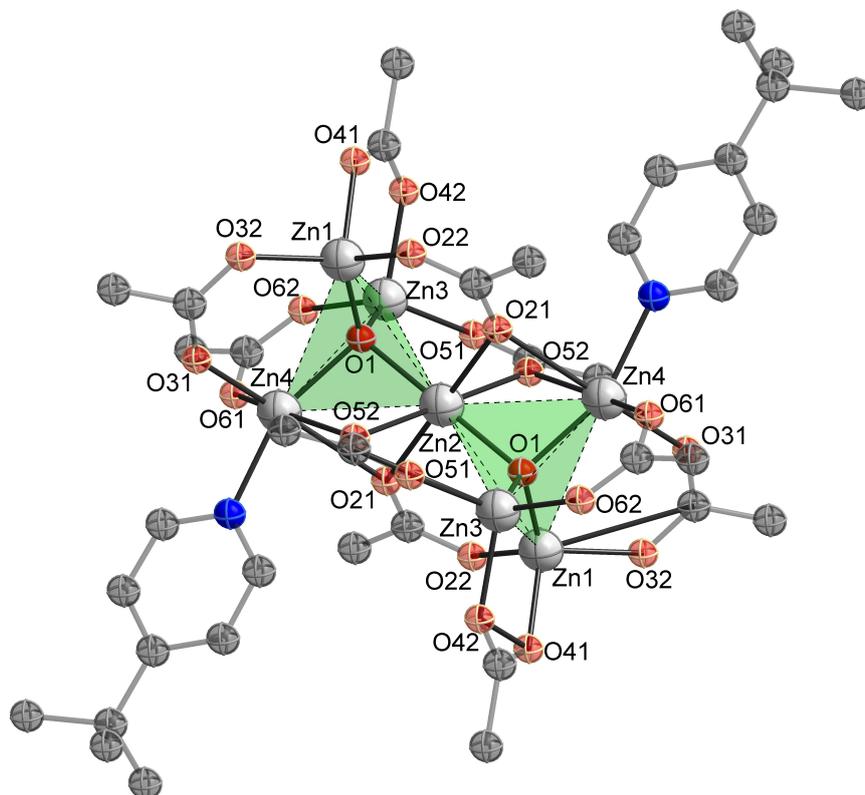
Treatment of  $[Zn_4(\mu^4-O)(O_2CCH_3)_6]$  with 1.0 equiv. of 4-tert-Butylpyridine leads quantitatively to cluster **1**, which is isolated as colourless crystals according to Scheme 1.



**Scheme 1.** Formation of  $[Zn_7O_2(O_2CCH_3)_{10}(4\text{-}^t\text{bupy})_2]$

Similar clusters had been synthesized before [5,6]. For instance the complex  $[\text{Zn}_7\text{O}_2(\text{O}_2\text{CCH}_3)_{10}(1\text{-Meim})_2]$  (1-Meim = 1-methylimidazole) has been isolated from the reaction of  $\text{Zn}(\text{OAc})_2$  and 1-methylimidazole in refluxing acetonitrile [7].

### 2.3. Crystal structure of $[\text{Zn}_7\text{O}_2(\text{O}_2\text{CCH}_3)_{10}(\text{bupy})_2]$



**Figure 1.** Molecular structure of  $[\text{Zn}_7\text{O}_2(\text{O}_2\text{CCH}_3)_{10}(\text{bupy})_2]$  (**1**); for clarity all hydrogen atoms, solvent molecules and minor components of the disorder have been omitted. Zn2 is located on a centre of inversion.

Figure 1 shows the central  $[\text{Zn}_7(\mu^4\text{-O}_2)]$  unit of the cluster in which the two central oxygen atoms are coordinated tetrahedrally by three zinc atoms and the one bridging Zinc atom which is connecting these two tetrahedra. Around this central unit there are 10 bridging acetate groups. 6 of them (labelled X3x, X4x, X6x and equivalents) bridge the edges of the tetrahedra opposite to central zinc (Zn2, on special position). The remaining 4 (X2x, X5x and

equivalents) connect the two tetrahedral units where one of the oxygen atoms of each is bridging two zinc atoms. The central Zinc atom is therefore coordinated octahedrally by 6 Oxygen atoms. The coordination number of the other zinc atoms is four. Two zinc atoms of each tetrahedron are surrounded by oxygen. One <sup>t</sup>bupy molecule is coordinated via nitrogen to one zinc atom of each [Zn<sub>4</sub>(μ<sup>4</sup>-O)] tetrahedron.

**Table 2**

Selected bond lengths (Å) and angles (deg) for [Zn<sub>7</sub>O<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>10</sub>(<sup>t</sup>bupy)<sub>2</sub>] **1**

*Bond lengths*

Zn(1)-O(1)(oxo)	1.921(2)	Zn(2)-O(1)(oxo)	1.971(2)
Zn(3)-O(1)(oxo)	1.913(2)	Zn(4)-O(1)(oxo)	1.962(2)
Zn(1)-O(22)	1.955(2)	Zn(1)-O(41)	1.977(2)
Zn(1)-O(32)	1.947(2)		
Zn(2)(cent.)-O(21)	2.128(2)	Zn(2)(cent.)-O(52)	2.189(2)
Zn(3)-O(51)	1.953(2)	Zn(3)-O(42)	1.979(2)
Zn(3)-O(62)	1.949(2)		
Zn(4)-O(31)	2.051(2)	Zn(4)-O(61)	2.036(3)
Zn(4)-N(11)	2.049(2)		
averaged Zn-Zn distance	3.165(7)		

*Bond angles*

Zn(1)-O(1)-Zn(2)	111.05(10)	Zn(2)-O(1)-Zn(3)	110.02(9)
Zn(1)-O(1)-Zn(3)	111.86(10)	Zn(2)-O(1)-Zn(4)	98.16(9)
Zn(1)-O(1)-Zn(4)	113.02(10)	Zn(3)-O(1)-Zn(4)	111.96(10)
O(1)-Zn(1)-O(22)	116.72(9)	O(1)-Zn(2)(cent.)-O(21)	98.16(8)
O(1)-Zn(1)-O(32)	114.87(9)	O(1)-Zn(2)(cent.)-O(52)	81.81(8)
O(1)-Zn(1)-O(41)	110.39(9)		
O(1)-Zn(3)-O(62)	112.95(9)	O(1)-Zn(4)-O(61)	102.94(9)
O(1)-Zn(3)-O(51)	120.67(9)	O(1)-Zn(4)-O(31)	101.83(8)
O(1)-Zn(3)-O(42)	108.92(9)	O(1)-Zn(4)-N(11)	156.37(10)
averaged O-C-O	124.9(3)		

### 3. Experimental

### 3.1 General remarks

All reactions were carried out under Argon atmosphere in Schlenkware. THF was distilled under Argon from sodium/benzophenone.

$[\text{Zn}_4(\mu^4\text{-O})(\text{O}_2\text{CCH}_3)_6]$  was prepared according to literature methods [2]. Infrared Spectra were recorded on a Nicolet 4700 FT-IR spectrometer [8].  $^1\text{H-NMR}$  Spectra were recorded on a Bruker DMX 300 Spectrometer.

Gas chromatographic determination of the transesterification yields was achieved using an Agilent 6890 N gas chromatograph with external calibration.

### 3.2 Preparation of $[\text{Zn}_7\text{O}_2(\text{O}_2\text{CCH}_3)_{10}(\textit{t}\text{bupy})_2]$ (2)

0.50 g (0.79 mmol) of  $\text{Zn}_4(\mu^4\text{-O})(\text{O}_2\text{CCH}_3)_6$  was dissolved in THF. To this solution 0.12 mL (0.79 mmol) 4-tert-Butylpyridine was added dropwise and the solution was kept stirring for 1 hour. A white precipitate formed and was filtered off. The solvent was removed in vacuum and the resulting white powder was solved in fluorobenzene. At 0 °C colorless crystals (0,48 g, 91 % yield) were obtained after 4 days.

IR (ATR  $\text{cm}^{-1}$ ): 2968, 2932, 2910, 2875, 1576, 1421, 1344, 1279, 1230, 1072, 1028, 833, 731, 671, 615, 567, 512, 478.

$^1\text{H NMR}$  (300 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  8.49 (d,  $^3J_{\text{HH}} = 6.2$  Hz, 4H  $\text{CH}_o$ ), 7.48 (d,  $^3J_{\text{HH}} = 6.2$  Hz, 4H  $\text{CH}_m$ ). 1.86 (s, 32H,  $\text{CH}_3\text{COO}$ ), 1.29 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).

$^{13}\text{C NMR}$  (75 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  178.7 ( $\text{COO}$ ), 149.6 ( $\text{C}_p$ ), 128.9 ( $\text{CH}_m$ ), 121.7  $\text{CH}_o$ , 35.1 ( $(\text{CH}_3)_3\text{C}$ ), 30.5 ( $(\text{CH}_3)_3\text{C}$ ), 23,4 ( $\text{CH}_3\text{COO}$ ).

Elemental analysis  $\text{C}_{38}\text{H}_{56}\text{O}_{22}\text{Zn}_7$  (C 33.79 %, H 4.18 %, N 2.07 %): C 34.1 %, H 4.41 %, N 1.79.

### 3.3 Transesterification of Methyl benzoate using $[\text{Zn}_4(\mu^4\text{-O})(\text{O}_2\text{CCH}_3)_6]$ as catalyst

Methyl benzoate (1.225 g, 9.0 mmol), 1-Decanol (1.709 g, 10.8 mmol) und  $[\text{Zn}_4(\mu^4\text{-O})(\text{O}_2\text{CCH}_3)_6]$  (284 mg,  $4.5 \cdot 10^{-4}$  mol) and  $^t\text{bupy}$  in different amounts were dissolved in 15 ml toluene and heated for 18h under reflux. Yield was determined using gas chromatography.

### 3.4 Polymerisation of lactid using $[\text{Zn}_7\text{O}_2(\text{O}_2\text{CCH}_3)_{10}(^t\text{bupy})_2]$ as catalyst

For the kinetic study 0.005 mmol of  $[\text{Zn}_7\text{O}_2(\text{O}_2\text{CCH}_3)_{10}(^t\text{bupy})_2]$  together with 1.000 mmol of *rac*-lactide were dissolved in 0.6 mL dichloromethane- $d_2$ .  $^1\text{H-NMR}$ -spectra were recorded every 24 hours. By integration of the significant doublet of lactide and the over time increasing, distorted and shifted doublet of polylactide, the turnover was determined.

### 3.5 X-ray crystallography

The crystals were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated  $\text{Mo}_{K\alpha}$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by Direct Methods (SHELXS-97)[9] and refined anisotropically by full-matrix least-squares on  $F^2$  (SHELXL-2014)[10]. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. The model includes two solvent molecules of which one is disordered. One of the *t*Bu residues is disordered.

## 4. Conclusions

$[\text{Zn}_4(\mu^4\text{-O})(\text{O}_2\text{CCH}_3)_6]$  is a useful catalyst for transesterification reaction. With equimolar amounts of  $^t\text{bupy}$  the cluster  $[\text{Zn}_7\text{O}_2(\text{O}_2\text{CCH}_3)_{10}(^t\text{bupy})_2]$  is formed quantitatively which leads to a lower activity in the transesterification reaction. In contrast to  $[\text{Zn}_4(\mu^4\text{-O})(\text{O}_2\text{CCH}_3)_6]$  the cluster  $[\text{Zn}_7\text{O}_2(\text{O}_2\text{CCH}_3)_{10}(^t\text{bupy})_2]$  catalyses also the polymerization of lactide.

## 5. Supplementary material

Anisotropic thermal parameters, hydrogen atom parameters, complete bond distances and angles, crystal data (cif) and all figures represented in ORTEP style (doc) are available from the authors. CIF file has also been deposited with the Cambridge Crystallographic Database as CCDC-1501391

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