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Synthesis and Crystal Structure of $(ZnEtOCy)_4$

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Abstract: One equivalent of cyclohexnol was added in one equivalent of toluene solution of diethyl zinc and the reaction mixture yielded the compound $(ZnEtOCy)_4$. The structure of $(ZnEtOCy)_4$ has confirmed discussed by single crystal x-ray diffraction studies.
Keywords: Synthesis, Crystal Structure of $(ZnEtOCy)_4$.

Introduction

Zinc containing materials like ZnO, ZnS, and zinc chalcogenides have attracted great attention due to their potential application in the field of optical, electrical, photovoltaic, catalysis and biological application.[1-5] The presence of wide band gap in ZnO and ZnS helps to construct the variety of optical devices.[6] Doping of other metal oxide, sulfide and chalcogenides with ZnO and ZnS resulted in different types of color emitting devices.[7] The availability of source for the preparation of ZnO and ZnS nanoparticles are limited. For instance different size of ZnO nanoparticles were synthesized by hydrolysis of $Zn(OAc)_2 \cdot 2H_2O$ in alcoholic medium[8] and some other zinc alkoxides/aryloxides.[9] The aim of the presented work is to establish a general synthetic approach to the preparation of single molecule precursor for preparation of ZnO nanoparticles.

Experimental

Material and Methods

All manipulations were performed either in an inert gas atmosphere of purified dry N_2 with standard Schlenk techniques or in an argon glove box. The glassware was dried at 130 °C, assembled hot and cooled under vacuum. All solvents were dried over appropriate alkali metals, distilled and degassed prior to use. Elemental analyses (C, H, N and S) were carried out at the Mikroanalytisches Labor, Institut für Anorganische Chemie, University of Goettingen.

Crystallography

The data of **1** was collected with a Bruker D8 three-circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Mo microsource with INCOATEC Quazar mirror optics.[10] The data were integrated with SAINT,[11] and an empirical absorption correction with SADABS was applied. The direct methods (SHELXS-97) was applied to solve the structure and refined against all data by full-matrix least-squares methods on F2 (SHELXL-97).[12] The hydrogen atoms were refined isotropically in calculated positions by using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Synthesis

Synthesis of $(ZnEtOCy)_4$ (1):

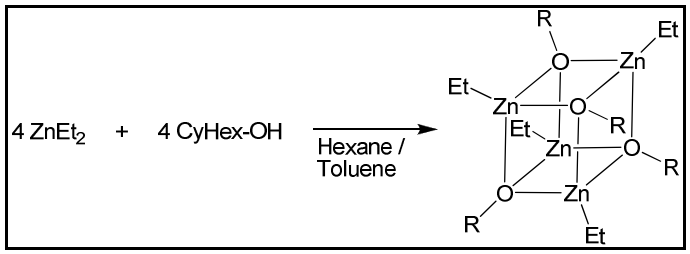
To the hexane (30 mL) solution of Cyclohexanol (4 mmole, 0.48 mL), $ZnEt_2$ (4 mmole, 0.41 mL) was added at room temperature. The resulting solution was stirred for 6 hrs and filtered using celite. The filtrate was

kept at -28 °C and colourless crystals were formed in 2 days. Yield 0.41 g (53 %). Anal.Calcd. for $C_{32}H_{64}O_4Zn_4$ (774.49) Found: C, 48.93; H, 8.06 requires C, 49.63; H, 8.33 %

Results and Discussion

Synthesis

Toluene solution of $ZnEt_2$ was treated with cyclohexylalcohol, in 1:1 ratio and the resulting mixture was stirred for six hours and filtered. The filtrate was kept at -28°C. The single crystals of terta nuclear organozinc cluster (**1**) was resulted from the filtrate.



Scheme 1: Synthesis of 1

Molecular Structures

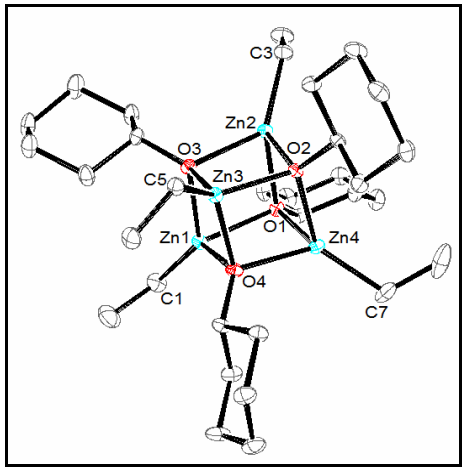


Figure 1: Molecular structure of 1 (All hydrogen atoms are omitted for clarity)

Single crystals of **1** were grown in hexane solution at -28 °C and a suitable one was subjected to the X-ray structural analysis. Compound **1** crystallized in the monoclinic space group *Pn* (the molecular structure of **1** is shown in Figure 1. The important bond distances and bond angles are shown in table 2. The molecular structure of **1** consists of four zinc atoms in tetrahedral form and zinc atoms are bonded to three oxygen atoms of cyclohexyl alkoxide which results the Zn_4O_4 cubane. The Zn-O bond distances are lies between 2.048 (4) to 2.092 (4) Å. The range of Zn_O_Zn bond angels is 94.54 to 98.02 °.

Table 1: Crystal data and structure refinement parameters of 1

Identification code	**1**
Empirical formula	C32 H64 O4 Zn4
Formula weight	774.39
Temperature	100(2) K
Crystal system, Space group	Monoclinic, *Pn*
Unit cell dimensions	*a* = 12.575(5) Å
	b = 9.988(5) Å
	c = 14.439(5) Å

	α = 90.0°
	β = 96.672(5)°
	γ = 90.0°
Volume	1801.2(13) Å^3
Z, Calculated density	2, 1.428 mg/m^3
Absorption coefficient	2.662 mm^{-1}
F(000)	816
Crystal size	0.08 x 0.06 x 0.03 mm^3
θ range for data collection	2.03 to 26.00°
Index ranges	-15<=h<=15, -12<=k<=12, -17<=l<=17
Reflections collected	40129
Independent reflections	7088 [R(int) = 0.0484]
Completeness to theta	100 %
Data / restraints / parameters	7088 / 2 / 365
Goodness-of-fit on F^2	1.043
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0409, wR2 = 0.1234
R indices (all data)	R1 = 0.0449, wR2 = 0.1280
Largest diff. peak and hole	0.602 and -0.465 e.Å^{-3}

Table 2: Bond distance and angles of 1

Bond distances (Å)			
Zn(1)-O(1)	2.068(4)	Zn(3)-O(1)	2.057(4)
Zn(1) -O(3)	2.059(4)	Zn(3) -O(3)	2.074(4)
Zn(1)-O(4)	2.073(4)	Zn(3)-O(4)	2.069(4)
Zn(1)-C(1)	1.964(6)	Zn(3)-C(3)	1.969(6)
Zn(2)-O(1)	2.055(4)	Zn(4)-O(1)	2.084(4)
Zn(2) -O(2)	2.092(4)	Zn(4) -O(2)	2.048(4)
Zn(2)-O(3)	2.086(40	Zn(4)-O(3)	2.081(4)
Zn(2)-C(2)	1.970(6)	Zn(4)-C(4)	1.963(6)
Bond angles (°)			
Zn(2)-O(1)-Zn(1)	98.02(15)	O(3)-Zn(1)-O(1)	82.29(15)
Zn(2)-O(1)-Zn(4)	96.56(15)	O(3)-Zn(1)-O(4)	83.46(15)
Zn(1)-O(1)-Zn(4)	94.61(15)	O(1)-Zn(1)-O(4)	85.09(15)
Zn(4)-O(2)-Zn(3)	97.85(15)	O(1)-Zn(2)-O(3)	81.95(15)
Zn(4)-O(2)-Zn(2)	96.53(15)	O(1)-Zn(2)-O(2)	82.85(15)
Zn(3)-O(2)-Zn(2)	95.75(15)	O(3)-Zn(2)-O(2)	83.16(14)
Zn(1)-O(3)-Zn(3)	96.52(15)	O(2)-Zn(3)-O(4)	82.69(15)
Zn(1)-O(3)-Zn(2)	97.34(16)	O(4)-Zn(3)-O(3)	83.19(15)
Zn(3)-O(3)-Zn(2)	95.41(16)	O(2)-Zn(3)-O(3)	84.29(14)
Zn(3)-O(4)-Zn(1)	96.25(16)	O(2)-Zn(4)-O(4)	82.63(15)
Zn(3)-O(4)-Zn(4)	96.46(15)	O(2)-Zn(4)-O(1)	83.23(15)
Zn(1)-O(4)-Zn(4)	94.54(15)	O(4)-Zn(4)-O(1)	84.51(15)

Summary

The tetra nuclear organozinc cluster was synthesized and characterized. The single crystal of **1** was analyzed and the important bond distances and angles were discussed.

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