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Base-stabilized dimeric organozinc alkoxides

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Index Abstract

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Single crystal X-ray analyses of two base-stabilized organozinc alkoxides [dmap-Zn(R)μ-OR]$_2$ R = Et **1**; *i*-Pr **2**), which were obtained from reactions of ZnR_2 and 4-dimethylaminopyridine (dmap) in the presence of O_2, are described.

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Abstract Dimeric, base-stabilized organozinc alkoxides [dmap-Zn(R)μ-OR]$_2$ R = Et **1**; *i*-Pr **2**), were obtained from reactions of ZnR_2 and 4-dimethylaminopyridine (dmap) in the presence of O_2. Their solid state structures were determined by single crystal X-ray diffraction studies. **1** is triclinic, space group *P-1* with a = 8.0639(10) Å, b = 8.3082(11) Å, c = 10.4545(13) Å, α = 70.846(2)°, β = 72.316(2)°, γ = 81.505(2)° and Z = 1. **2** is triclinic, space group *P-1* with a = 8.6381(6) Å, b = 9.2773(7) Å, c = 10.2186(7) Å, α = 112.094(1)°, β = 103.040(1)°, γ = 92.598(1)° and Z = 1.

Keywords Lewis-base · Lewis acid · X-ray crystal structure

Short title: Base-stabilized organozinc alkoxide

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Introduction

Zinc organometallic compounds, which were initially synthesized by Frankland almost 150 years ago [1], are valuable reagents for various applications. Alkylzinc halides are used for Simmons–Smith cyclopropanation [2], nickel-catalyzed Negishi reactions [3] and in polymerisation reactions of olefins [4]. Moreover, zinc alkoxides have been shown to effectively catalyze ring-opening polymerizations of lactide [5,6,7,8], esters and ethers [9,10,11] and copolymerisation of epoxides with CO_2 [12,13]. However, one of the earliest reactions studied in organozinc chemistry is that of zinc alkyl complexes with dioxygen. Frankland reported in 1849 on the reaction of $ZnEt_2$ with O_2, that occurred with formation of the bisalkoxide $Zn(OEt)_2$,[14] whereas Butlerov [15] and Lissenko [16] reported on the formation of the partly oxygenated species Zn(Et)OEt. In 1890 Demuth and Meyer demonstrated that the O_2 molecule initially inserts into the Zn-C bond with subsequent formation of the alkylperoxide Zn(Et)OOEt.[17] Since then, oxygenation reactions of several ZnR_2 have been investigated and the resulting complexes have been structurally characterized.[18] Recently, Lewinski et al. showed that $ZnMe_2$ reacts with O_2 with selective insertion of an oxygen atom into a single Zn-C bond and formation of $Me_6Zn_7(OMe)_8$,[19] whereas the reaction of *t*-Bu_2Zn with O_2 either yielded the alkoxide [(thf)Zn(*t*-Bu)O*t*-Bu]$_2$ or the peroxide complexe [(4-MePy)Zn(*t*-Bu)O*t*-Bu]$_2$, depending on the Lewis base added (thf or 4-methylpyridine).[20]

We herein present the synthesis and single crystal X-ray structures of the two base-stabilized alkylzinc alkoxides [dmapZn(R)-μ-OR]$_2$ (dmap = 4-dimethylaminopyridine; R = Et **1**, *i*-Pr **2**), which were obtained from reactions of ZnR_2 with dmap in the presence of oxygen. ZnR_2 was dissolved in pentane and a solution of one equivalent dmap in pentane was added. After the reaction mixture was stirred for 30 min at ambient temperature under nitrogen, dry oxygen was bubbled through the solution for 2 minutes.

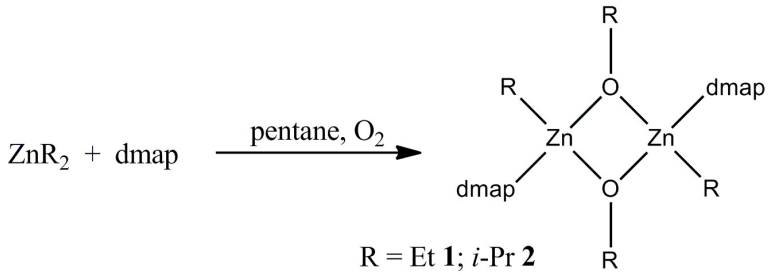

Figure 1 Synthesis of [dmapZn(R)-μ-OR]$_2$ (R = Et **1**, *i*-Pr **2**).

Crystallization of **1** and **2**

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Solutions of 0.5 g **1** and **2** in 3 mL of *n*-pentane were stored at -30 °C. Single crystals suitable for a single crystal X-ray analyses were obtained after 2 weeks. Table 1 illustrates the crystal data and structure refinement of **1** and **2**.

((Table 1 here))

Crystal structures of **1** and **2**

Data were collected on a Bruker SMART Apex-CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at T = 120(2) K and the structures were solved by Direct Methods and refined by full-matrix least-squares on F^2. Semi-empirical absorption corrections from equivalents were applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located from ΔF maps and refined at idealized positions using a riding model with $U_{iso}(H)$ = 1.2 $U_{eq}(C)$ or 1.5 U_{eq}(C-methyl) [21]. CCDC-773619 (**1**) and CCDC-773620 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by contacting The Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk.

Results and Discussion

Complexes **1** and **2** are formed by selective insertion of an oxygen atom into only one Zn-R bond of the initially formed adducts R_2Zn(dmap). The resulting dmap-stabilized zinc alkoxides of the type dmap-Zn(R)OR subsequently dimerize with formation of the alkoxide bridged complexes $[dmapZn(R)\text{-}\mu\text{-}OR]_2$ (R = Et **1**, *i*-Pr **2**), respectively. In contrast, Lewinski et al. obtained the bisperoxide complex $[4\text{-}MePyZn(t\text{-}Bu)OOt\text{-}Bu]_2$ from the reaction of $t\text{-}Bu_2Zn$ with O_2 in the presence of 4-methylpyridine.[20] Both **1** and **2** crystallize in the triclinic space group P-1, the molecules lie on crystallographic inversion centers each. Single crystals were obtained from pentane solutions of **1** and **2** after storage for two weeks at –30 °C. Central structural moiety in both compounds is the planar four-membered Zn_2O_2 ring. The Zn atoms are additionally coordinated by a dmap Lewis-base, hence adopting a distorted tetrahedral environment.

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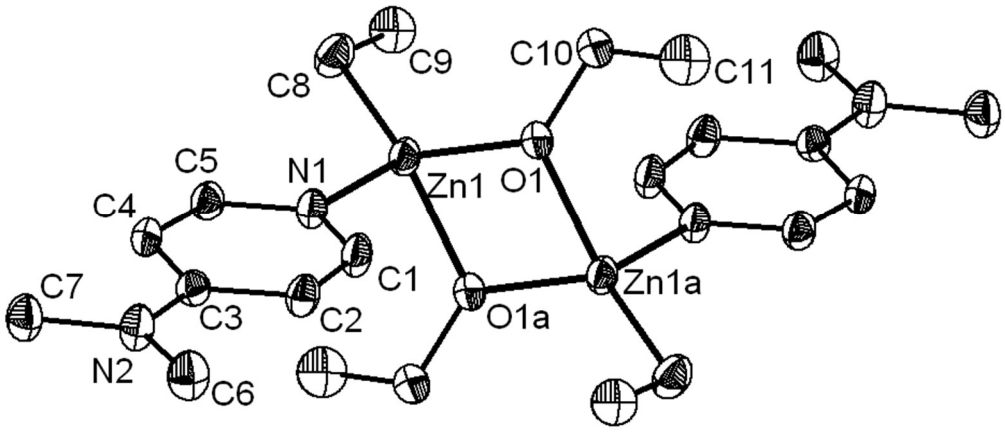

Figure 2 The molecular structure and atom-numbering scheme for [dmapZn(Et)-μ-OEt]$_2$ **1**. Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

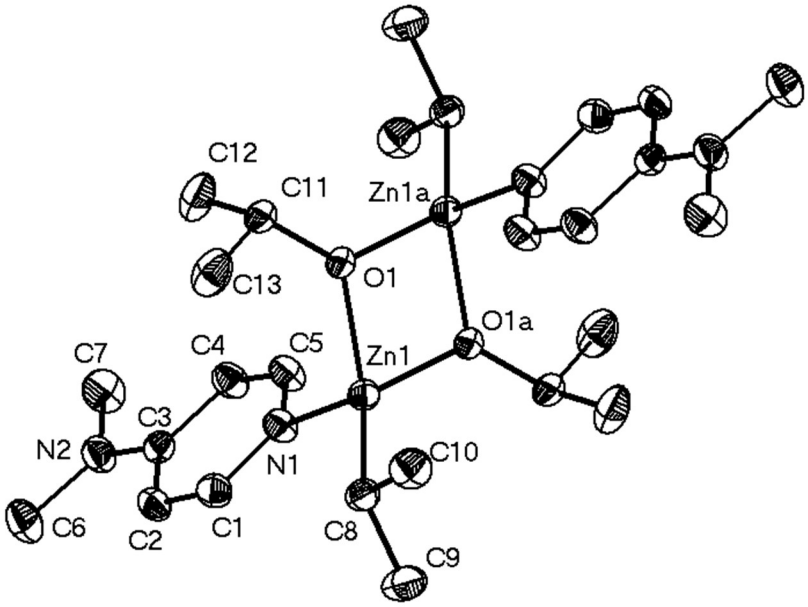

Figure 3 The molecular structure and atom-numbering scheme for [dmapZn(*i*-Pr)-μ-O*i*-Pr]$_2$ **2**. Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

The Zn-O (av. 2.000(2) **1**, 1.989(1) **2** Å) and Zn-C bond lengths (1.986(2) **1**, 2.000(2) Å **2**) are within the expected range. The Zn-N bond lengths, which are almost identical (2.100(2) **1**, 2.111(2) Å **2**), are also typical for this type of compound. Pyridine-stabilized alkylzinc alkoxide complexes, which were recently reported [22], show comparable structural parameters. The different Zn-O-Zn (97.9(1) **1**; 99.7(1)° **2**) and O-Zn-O bond angles (82.1(1) **1**; 80.3(1)° **2**) reflect the different steric demand of the alkyl substituents bound to the Zn atoms. *i*-Pr groups are sterically bulkier substituent compared to Et groups, hence decreasing the endocyclic O-Zn-O and increasing the Zn-O-Zn and bond angles.

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Table 1 Crystal data and structure refinement of **1**

CCDC deposit no.	773619	773620
Empirical formula	$C_{22}H_{40}N_4O_2Zn_2$	$C_{26}H_{48}N_4O_2Zn_2$
Formular weight	523.32	579.42
Temperature	120(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	triclinic
Space group	P-1	P-1
Unit cell dimensions	a = 8.0639(10) Å	a = 8.6381(6) Å
	b = 8.3082(11) Å	b = 9.2773(7) Å
	c = 10.4545(13) Å	c = 10.2186(7) Å
	α = 70.846(2)°	α = 112.094(1)°
	β = 72.316(2)°	β = 103.040(1)°
	γ = 81.505(2)°	γ = 92.598(1)°
Volume	629.48(14) $Å^3$	731.47(9) $Å^3$
Z	1	1
Density (calculated)	1.381 Mg m^{-3}	1.315 Mg m^{-3}
Absorption coefficient	1.929 mm^{-1}	1.667 mm^{-1}
F(000)	276	308
Crystal size	0.38 x 0.35 x 0.27 mm	0.35 x 0.27 x 0.22 mm
Theta range for data collection	27.88°	28.08°
Index range	$-10 \le h \le 10, -10 \le k \le 10, -13 \le l \le 13$	$-11 \le h \le 11, -12 \le k \le 12, -13 \le l \le 11$
Reflections collected	6058	7365
Independent reflections	2983 (R_{int} = 0.0197)	3518 (R_{int} = 0.0224)
Completeness to theta = 56°	98.9%	98.5%
Max. and min. transmission	0.6240 and 0.5277	0.7106 and 0.5931
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2983/0/126	3518/0/154
goodness-of-fit on F^2	1.050	1.056
Final *R* indices [$I > 2\text{sigma}(I)$]	$R1$ = 0.0355, $wR2$ = 0.0889	$R1$ = 0.0299, $wR2$ = 0.0734
R indices (all data)	$R1$ = 0.0402, $wR2$ = 0.0913	$R1$ = 0.0341, $wR2$ = 0.0735
Largest diff. peak and hole	0.870 and -0.680 e $Å^{-3}$	0.494 and -0.221 e $Å^{-3}$

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Table 2. Selected geometric parameters (Å, °).

1		**2**	
Zn1-O1	1.9883(16)	Zn1-O1	1.9906(12)
Zn1-O1a	2.0111(16)	Zn1-O1a	1.9873(12)
Zn1-C8	1.986(2)	Zn1-C8	2.0000(18)
Zn1-N1	2.1000(19)	Zn1-N1	2.1109(15)
O1-C10	1.400(3)	O1-C11	1.408(2)
O1-Zn1-O1a	82.12(7)	O1-Zn1-O1a	80.32(5)
Zn1-O1-Zn1a	97.88(7)	Zn1-O1-Zn1a	99.68(5)
O1-Zn1-N1	98.67(7)	O1-Zn1-N1	102.43(6)
O1-Zn1-C8	128.25(9)	O1-Zn1-C8	128.00(7)
C8-Zn1-N1	114.48(9)	C8-Zn1-N1	112.91(7)

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