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# Synthesis and structures of zinc alkoxo, aryloxo and hydroxo complexes with an amidodiamine ligand

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ABSTRACT

The synthesis and characterization of zinc complexes bearing an amidodiamine ligand, $(EtO)_4Zn_3[N(CH_2CH_2NMe_2)_2]_2$ (**1**), $[(Et_3CO)ZnN(CH_2CH_2NMe_2)_2]_2$ (**2**) and $[(2,6\text{-}^iPr_2C_6H_3O)ZnN(CH_2CH_2NMe_2)_2]_2$ (**3**), $[(Me_3Si)_2N]Zn[N(CH_2CH_2NMe_2)_2]$ (**4**) and $[(Me_3Si)_2N]_2Zn_2(OH)[N(CH_2CH_2NMe_2)_2]$ (**5**), are reported. Compounds **1**–**3** are synthesised in the reactions of $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2$ with 2 equiv. of ethanol, 3-ethyl-3-pentanol and 2,6-diisopropylphenol, respectively. Compound **4** is obtained by the reaction of $Zn[N(SiMe_3)_2]_2$ with $HN(CH_2CH_2NMe_2)_2$, and compound **5** is synthesised by reacting **4** with 1 equiv. of $H_2O$. Compound **4** is characterized by NMR and MS while all of the other compounds are characterized with NMR, MS, elemental analysis and single-crystal X-ray diffraction. Compound **1** is a trinuclear species containing a $Zn_3N_2O_2$ core. Compounds **2** and **3** are dimeric with planar $Zn_2N_2$ rings. Compound **5** is dimeric with a planar $Zn_2NO$ ring.

## 1. Introduction

Zinc alkyls such as diethyl zinc are the most widely used precursors in vapor phase deposition of ZnO films. Because zinc alkyls are pyrolytic, alternative precursors including carbarmates such as $Zn_4O(CO_2NEt_2)_6$ [1,2], zinc acetylacetonate derivatives [3,4], β-ketoiminates and β-iminoesterates [5], alkyl zinc alkoxides such as $(MeZnO^iPr)_4$ and $(MeZnO^tBu)_4$ [6] and a methyl zinc aminoalkoxide [7] have been adopted in the ZnO film preparation.

The dialkoxides $Zn(OR)_2$ [8] and diamides $Zn(NR_2)_2$ [9,10] with short-chain alkyl R groups, presumably polymeric, are nonvolatile and insoluble. Soluble dialkoxides [11–19] and diamides [20–29], typically having a monomeric or dimeric structure, are obtained using bulky ligands. Most of them have a low volatility. Exceptions are the bis(trimethylsilyl)amido zinc complexes, such as $Zn[N(SiMe_3)_2]_2$ [26] that is volatile and has been used in the deposition of $SiO_2$-containing ZnO films [30] and $Zn_3N_2$ films [31].

In contrast to the dialkoxides, alkyl zinc alkoxides are soluble even for the smallest alkyl groups [9,32–34] and some, as indicated above, are volatile. These compounds have also been used in nanocrystalline ZnO synthesis [35–39]. Analogously, a number of soluble and/or volatile alkyl zinc amide compounds exist [10,40–42]. Their applications in materials synthesis have yet to be explored.

Only a few Zn complexes bearing both amido and alkoxy ligands were reported, and all contain bulky ligands [12,43,44]. To study the ZnO precursor chemistry in this group of compounds, we react $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2$ [45] with a series of alcohols to obtain several crystalline compounds having an alkoxy or aryloxy ligand and the amidodiamine ligand $N(CH_2CH_2NMe_2)_2$. The synthesis and structures of these compounds are reported in this paper. The $N(CH_2CH_2NMe_2)_2$ ligand and its corresponding amine $HN(CH_2CH_2NMe_2)_2$ were previously used in the preparation of volatile Al, Ga and Sr compounds [46–48]. Several Zn complexes bearing this ligand were also reported [45], one of which, the diamide $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2$, is used as a reactant in the present study. It is prepared by ligand exchange from $[Zn(N^iBu_2)_2]_2$ [45]. We have also attempted the reaction of $Zn[N(SiMe_3)_2]_2$ with $HN(CH_2CH_2NMe_2)_2$ and only the mono-substituted complex, $[(Me_3Si)_2N]Zn[N(CH_2CH_2NMe_2)_2]$, is obtained. Interestingly, this complex reacts with $H_2O$ forming a hydroxo Zn complex in a moderate yield.

## 2. Experimental

### 2.1. Materials and general procedures

The solvents and reactants are obtained from Aldrich. Toluene and hexanes are dried with alumina in an MBraun solvent purification system. Diethyl ether, pentane, diisobutylamine, benzene-$d_6$, toluene-$d_8$ and deuterated chloroform are dried over calcium hydride under nitrogen. Ethanol and 3-ethyl-3-pentanol ($Et_3COH$) are dried over 4 A molecular sieves and 2,6-diisopropylphenol ($2,6\text{-}^iPr_2C_6H_3OH$) is recrystallized from pentane at −50 °C. $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2$ [45] and $Zn[N(SiMe_3)_2]_2$ [49] are prepared according to the methods described in the literature. All

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experiments are conducted under an oxygen-free, dry-nitrogen atmosphere using standard Schlenk and glovebox techniques.

Except for the otherwise indicated, all NMR spectra are obtained in benzene-$d_6$ solutions at room temperature on a Varian INOVA 300 spectrometer. The residual proton at 7.15 ppm and the carbon resonance at 128.39 ppm in benzene-$d_6$ are used as the internal standards for $^1H$ and $^{13}C$ NMR, respectively. When $CDCl_3$ is used as the NMR solvent, the residual proton at 7.27 ppm and the carbon resonance at 77.23 ppm in $CDCl_3$ are the internal standards. When toluene-$d_8$ is used as the solvent, one of the residual aromatic protons at 7.00 ppm and one carbon resonance at 137.86 ppm are used as the internal standards. The IR spectra (KBr pellets) are recorded on a Nicolet MAGNA-IR 560 spectrometer. Chemical-ionization (CI) mass spectra are acquired on a Finnigan Mat 95 spectrometer using a direct insertion probe. The samples are evaporated at 150 °C and the ionization gas mixture is methane with 4% ammonia. Melting points are measured in sealed glass capillaries and were uncorrected. The elemental analyses are performed by Columbia Analytical Services, Tucson, AZ.

### *2.2. Synthesis of $(EtO)_4Zn_3[N(CH_2CH_2NMe_2)_2]_2$ (**1**)*

To a stirred solution of $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2$ (2.50 g, 3.28 mmol) in 30 mL of toluene at room temperature is added EtOH (0.30 g, 6.6 mmol) via a syringe. A white solid formed upon the addition of EtOH, which is quickly dissolved affording a colorless solution. The solution is stirred for 2 h. The volatiles are then removed under vacuum affording a wet, white solid. Pentane (30 mL) is added to dissolve the solid and filtered. After the filtrate is concentrated to ca. 8 mL and stored at −20 °C for a few days, colorless, crystalline compound **1** precipitates and is isolated (1.05 g, 70% yield). M.p.: 88.0–90.0 °C. $^1H$ NMR: $\delta$ 1.48 (6H, t, $CH_2CH_3$), 1.67 (6H, t, $CH_2CH_3$), 2.30 (24H, s, $NMe_2$), 2.00, 2.46, 2.79 and 2.97 (total 16H, overlapping broad multiplets, $CH_2CH_2NMe_2$), 4.18 (4H, q, $CH_2CH_3$), 4.51 (4H, q, $CH_2CH_3$). $^{13}C$ NMR: $\delta$ 22.3 and 24.7 ($CH_2CH_3$), 45.7 ($NMe_2$), 52.8 (broad, $CH_2NMe_2$), 60.8 (broad, $CH_2CH_2NMe_2$), 62.4 and 64.0 ($CH_2CH_3$). CI MS (assignment, % relative intensity): 693 ($[\mathbf{1}+H]^+$, 2.1), 647 ($[\mathbf{1}-OEt]^+$, 12), 537 ($[\mathbf{1}-Zn(OEt)_2+H]^+$, 21), 491 ($[\mathbf{1}-Zn(OEt)_2-OEt]^+$, 26), 381 ($\{Zn[N(CH_2CH_2NMe_2)_2]_2+H\}^+$, 58), 378 ($[\mathbf{1}-Zn(OEt)_2-N(CH_2CH_2NMe_2)_2]^+$, 23), 268 ($[(EtO)ZnN(CH_2CH_2NMe_2)_2+H]^+$, 17), 160 ($[H_2N(CH_2CH_2NMe_2)_2]^+$, 100). *Anal.* Calc. for $C_{24}H_{60}N_6O_4Zn_3$: C, 41.56; H, 8.73; N, 12.13. Found: C, 41.50; H, 8.85; N, 12.26%.

### *2.3. Synthesis of $[(Et_3CO)ZnN(CH_2CH_2NMe_2)_2]_2$ (**2**)*

To a stirred solution of $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2$ (1.20 g, 1.57 mmol) in 30 mL of toluene at room temperature is added $Et_3COH$ (0.37 g, 3.1 mmol) via a syringe. A clear solution forms and is stirred for 2 h. Volatiles are then removed under vacuum to afford a white solid. Pentane (20 mL) is added to dissolve the solid. After the pentane solution is stored at −20 °C overnight, colorless, crystalline compound **2** precipitates and is isolated (0.53 g, 50% yield). M.p.: 70.0–73.0 °C. $^1H$ NMR (in toluene-$d_8$, 22 °C): $\delta$ 0.86, 1.01 and 1.05 (total 18H, overlapping multiplets, $CH_2CH_3$), 1.25, 1.45 and 1.58 (total 12H, overlapping multiplets, $CH_2CH_3$), 2.05, 2.12, and 2.24 (total 24H, overlapping broad singlets, $NMe_2$), 2.40, 2.70, 2.96 and 3.20 (total 16H, overlapping broad multiplets, $CH_2CH_2NMe_2$). $^{13}C$ NMR: $\delta$ 9.8, 10.3 and 10.6 ($CH_2CH_3$), 33.8 and 35.5 ($CH_2CH_3$), 45.9, 46.7 (broad) and 47.0 ($NMe_2$), 51.7, 52.2, 53.8 and 55.6 ($CH_2NMe_2$), 52.3, 62.8 (broad), 63.1 and 64.8 ($CH_2CH_2NMe_2$), 72.6 (broad) and 73.0 ($OCEt_3$). The low-temperature NMR results will be discussed below. CI MS (assignment, % relative intensity): 679 ($[\mathbf{2}+H]^+$, 0.8), 563 ($[\mathbf{2}-OCEt_3]^+$, 14), 520 ($[\mathbf{2}-N(CH_2CH_2NMe_2)_2]^+$, 100), 381 ($[\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2+H]^+$, 73), 338 ($[(Et_3CO)ZnN(CH_2CH_2NMe_2)_2+H]^+$, 24), 322 ($[(Et_3CO)ZnN(CH_2CH_2NMe_2)_2-Me]^+$, 12), 160 ($[H_2N(CH_2CH_2NMe_2)_2]^+$, 36). *Anal.* Calc. for $C_{30}H_{70}N_6O_2Zn_2$: C, 53.17; H, 10.41; N, 12.40. Found: C, 52.88; H, 10.74; N, 12.62%.

### *2.4. Synthesis of $[(2,6\text{-}{}^iPr_2C_6H_3O)ZnN(CH_2CH_2NMe_2)_2]_2$ (**3**)*

To a stirred solution of $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2$ (1.20 g, 1.57 mmol) in 40 mL of toluene at room temperature is added $2,6\text{-}{}^iPr_2C_6H_3OH$ (0.56 g, 3.1 mmol) via a syringe. A clear solution forms and is stirred for 2 h. After the solution is concentrated to 10 mL and stored at −20 °C, colorless, crystalline compound **3** precipitates and is isolated (0.60 g). The toluene and as-formed $HN(CH_2CH_2NMe_2)_2$ in the mother liquor are removed under vacuum, and 4 mL of toluene is added to dissolve the residue. The solution is stored at −20 °C for a few days to yield a second crop of the product. A total yield of 0.66 g (50% yield) of compound **3** is obtained. M.p.: 210 °C, decomposed. $^1H$ NMR: $\delta$ 1.44 (24H, d, $CHMe_2$), 2.05 (24H, s, $NMe_2$), 2.37 (8H, t, $CH_2NMe_2$), 2.97 (8H, t, $CH_2CH_2NMe_2$), 3.61 (4H, heptet, $CHMe_2$), 6.97 (2H, t, *para*-H in $C_6H_3O$), 7.26 (4H, d, *meta*-H in $C_6H_3O$). $^{13}C$ NMR: $\delta$ 24.2 ($CHMe_2$), 28.0 ($CHMe_2$), 46.3 ($NMe_2$), 52.6 ($CH_2NMe_2$), 62.0 ($CH_2CH_2NMe_2$), 115.9 (*para*-C in $C_6H_3O$), 123.2 (*meta*-C in $C_6H_3O$), 136.8 (*ortho*-C in $C_6H_3O$), 162.1 (C bonded to O in $C_6H_3O$). *Anal.* Calc. for $C_{40}H_{74}N_6O_2Zn_2$: C, 59.91; H, 9.30; N, 10.48. Found: C, 60.04; H, 9.30; N, 10.71%.

### *2.5. Synthesis of $[(Me_3Si)_2N]Zn[N(CH_2CH_2NMe_2)_2]$ (**4**)*

To a stirred solution of $Zn[N(SiMe_3)_2]_2$ (2.00 g, 5.18 mmol) in 10 mL of $Et_2O$ at room temperature is added a solution of $HN(CH_2CH_2NMe_2)_2$ (0.825 g, 5.18 mmol) in 10 mL of $Et_2O$. A clear solution forms and is stirred for 1 h. The volatiles are removed under vacuum affording an oil. The $^1H$ NMR spectrum of this crude product shows that over 90% is compound **4**. Hexanes (10 mL) are added to dissolve the oil. Upon cooling at −78 °C, colorless needles precipitate from the solution and are isolated at low temperatures. When warmed to room temperature, the crystalline material melts to a colorless liquid, which slowly solidifies over a period of 24 h to yield a colorless, glassy solid (1.42 g, 71% yield). M.p.: 49.0–62.0 °C. $^1H$ NMR: $\delta$ 0.30 (18H, s, $SiMe_3$), 1.96 (12H, s, $NMe_2$), 2.27 (4H, t, $CH_2NMe_2$), 3.05 (4H, t, $CH_2CH_2NMe_2$). $^{13}C$ NMR: $\delta$ 6.3 ($SiMe_3$), 45.0 ($NMe_2$), 52.3 ($CH_2NMe_2$), 62.5 ($CH_2CH_2NMe_2$). CI MS (assignment, % relative intensity): 770 ($\{Zn[N(SiMe_3)_2]_2\}_2^+$, 0.2), 768 ($\{[(Me_3Si)_2N]Zn[N(CH_2CH_2NMe_2)_2]\}_2^+$, 0.2), 612 ($\{Zn_2[N(SiMe_3)_2]\}_3^+$, 0.5), 449 ($\{[(Me_3Si)_2N]Zn_2[N(CH_2CH_2NMe_2)_2]-H\}^+$, 1.5), 384 ($Zn[N(SiMe_3)_2]_2^+$, 2.0), 382 ($\{[(Me_3Si)_2N]Zn[N(CH_2CH_2NMe_2)_2]\}^+$, 2.0), 380 ($\{Zn[N(CH_2CH_2NMe_2)_2]_2\}^+$, 2.0), 369 ($\{Zn[N(SiMe_3)_2]_2-Me\}^+$, 20), 324 ($\{[(Me_3Si)_2N]Zn[N(CH_2CH_2NMe_2)_2]-CH_2NMe_2\}^+$, 70), 275 ($\{[(Me_3Si)_2N]Zn(NH_3)_3\}^+$, 85), 224 ($\{Zn[N(SiMe_3)_2]\}^+$, 70), 146 ($\{HN(SiMe_3)_2-Me\}^+$, 95),130 ($NSi_2Me_4^+$, 98), 72 ($CH_2CH_2NMe_2^+$, 83), 58 ($SiMe_2^+$, 100).

### *2.6. Synthesis of $[(Me_3Si)_2N]_2Zn_2(OH)[N(CH_2CH_2NMe_2)_2]$ (**5**)*

To a stirred solution of $Zn[N(SiMe_3)_2]_2$ (2.02 g, 5.23 mmol) in 10 mL of $Et_2O$ at room temperature is added a solution of $HN(CH_2CH_2NMe_2)_2$ (0.833 g, 5.23 mmol) in 10 mL of $Et_2O$. A clear solution forms and is stirred for 1 h. Then the solvent and as-formed $HN(SiMe_3)_2$ are removed under vacuum. Toluene (20 mL) is added to dissolve the residue. The solution is cooled at −78 °C and $H_2O$ (0.094 mL, 5.2 mmol) is added via a syringe. The mixture is warmed to room temperature and stirred for 1.5 h to yield a cloudy solution. Filtration removes a solid (0.43 g), which is not characterized. The volatiles in the filtrate are removed under vacuum and the residue is dissolved in 10 mL of pentane. Upon cooling at −78 °C, colorless, crystalline compound **5** precipitates and is isolated (0.68 g, 42%). M.p.: 148.0–150.0 °C. IR: $\nu_{OH}$, 3709 cm$^{-1}$. CI MS (assignment, % relative intensity): 610 ([**5**$-$OH]$^+$, 5.5), 465 ([**5**$-$N(SiMe$_3$)$_2$]$^+$, 19), 162 ([(Me$_3$Si)$_2$NH$_2$]$^+$, 100), 160 ([H$_2$N(CH$_2$CH$_2$NMe$_2$)$_2$]$^+$, 52). *Anal.* Calc. for $C_{20}H_{57}N_5OSi_4Zn_2$: C, 38.32; H, 9.16; N, 11.17. Found: C, 38.08; H, 9.05; N, 11.05%. $^1$H NMR (in C$_6$D$_6$, 22 °C): $\delta$ 0.28 (36H, s, SiMe$_3$), 1.96 (16H, broad s, NMe$_2$ and C*H*$_2$NMe$_2$), 2.64 (4H, broad s, C*H*$_2$CH$_2$NMe$_2$). $^{13}$C NMR (in C$_6$D$_6$, 22 °C): $\delta$ 6.8 (SiMe$_3$), 45.1 and 48.2 (broad peaks, NMe$_2$), 50.5 (*C*H$_2$NMe$_2$), 62.6 (*C*H$_2$CH$_2$NMe$_2$). $^1$H NMR (in CDCl$_3$, 22 °C): $\delta$ 0.01 (36H, s, SiMe$_3$), 2.41 (12H, broad s, NMe$_2$), 2.66 (4H, broad s, C*H*$_2$NMe$_2$), 2.89 (4H, broad s, C*H*$_2$CH$_2$NMe$_2$). $^{13}$C NMR (in CDCl$_3$): 22 °C: $\delta$ 6.2 (SiMe$_3$), 45.5 and 48.1 (broad peaks, NMe$_2$), 50.1 (*C*H$_2$NMe$_2$), 62.6 (*C*H$_2$CH$_2$NMe$_2$); 0 °C: $\delta$ 6.1 (SiMe$_3$), 45.2 and 48.5 (NMe$_2$), 50.0 (*C*H$_2$NMe$_2$), 62.3 (*C*H$_2$CH$_2$NMe$_2$); $-$20 °C: $\delta$ 6.1 (SiMe$_3$), 45.1 and 48.4 (NMe$_2$), 49.9 (*C*H$_2$NMe$_2$), 62.2 (*C*H$_2$CH$_2$NMe$_2$); $-$40 °C: $\delta$ 6.0 (SiMe$_3$), 45.0 and 48.4 (NMe$_2$), 49.8 (*C*H$_2$NMe$_2$), 62.0 (*C*H$_2$CH$_2$NMe$_2$).

### 2.7. X-ray data collection, structure solution and refinement

The detailed experimental procedures and structure solution methods are described elsewhere [50]. A Siemens Smart system is used for compounds **1** and **3** and a Bruker Smart system is used for compounds **2** and **5**. The final cell constants are calculated from 3987 strong reflections for **1**, 2491 for **2**, 3573 for **3**, and 2540 for **5**. For all structures, all non-hydrogen atoms are refined with anisotropic displacement parameters. All hydrogen atoms are placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. For the OH group in compound **5**, the largest difference Fourier peak in the E-map (without the H) is ca. 0.6 Å from the oxygen atom. In the modeling, the hydroxyl proton is placed on the twofold axis at 0.84 Å from the O atom. For compound **1**, each of the ethoxy groups O(1)–C(17)–C(18) and O(4)–C(23)–C(24) is modeled as disordered over two positions with occupancy ratios of 52:48 and 92:8, respectively. The experimental conditions and unit cell information for compounds **1**–**3** and **5** are summarized in Table 1.

## 3. Results and discussion

### 3.1. Synthesis and characterization of compounds 1–3

Compounds **1**–**3** are isolated in good yields from the reactions of {Zn[N(CH$_2$CH$_2$NMe$_2$)$_2$]$_2$}$_2$ with 2 equiv. of ethanol, 3-ethyl-3-pentanol and 2,6-diisopropylphenol (Scheme 1), and are characterized using NMR, IR, MS, elemental analysis and single-crystal X-ray diffraction.

The three compounds are colorless crystalline materials soluble in nonpolar and weakly polar organic solvents. They do not sublime when heated to 100 °C under vacuum. The elemental analyses of the three compounds are satisfactory, and the chemical ionization mass spectra for compounds **1** and **2** exhibit the molecular ions (plus 1).

The $^1$H and $^{13}$C NMR spectra of compound **3** show a set of N(CH$_2$CH$_2$NMe$_2$)$_2$ and 2,6-$^i$Pr$_2$C$_6$H$_3$O resonances, consistent with its X-ray crystal structure given below. The NMR results for compounds **1** and **2**, however, differ from those expected based on their X-ray crystal structures. For **1**, while the bridging and terminal EtO ligands are clearly identified by two sets of $^1$H and $^{13}$C resonances, the $^1$H and $^{13}$C NMR peaks of the N(CH$_2$CH$_2$NMe$_2$)$_2$ ligands are substantially broadened. This is perhaps due to the existence of a dynamic process involving the NMe$_2$ bonding and nonbonding to Zn. Variable temperature NMR spectra of compound **2** are collected in toluene-*d*$_8$ from room temperature to $-$85 °C. In all $^1$H and $^{13}$C spectra, multiple broad, overlapping N(CH$_2$CH$_2$NMe$_2$)$_2$ resonances exist. From the relatively better resolved OCEt$_3$ peaks, we can estimate that more than three isomers of **2** exist at all temperatures. Specifically, according to the crystal structure of **2** shown below, the OCEt$_3$ ligand should only afford one set of resonances, but in all $^1$H spectra, at least three sets of resonances are observed and the relative intensities vary with the temperatures. We are not able to assign the structures of these isomers. In view of the bulkiness of the OCEt$_3$ ligand, it is possible that three-coordinate Zn isomers are present in solution as a result of dissociation of the NMe$_2$ group from Zn. In addition, monomers of **2** could exist.

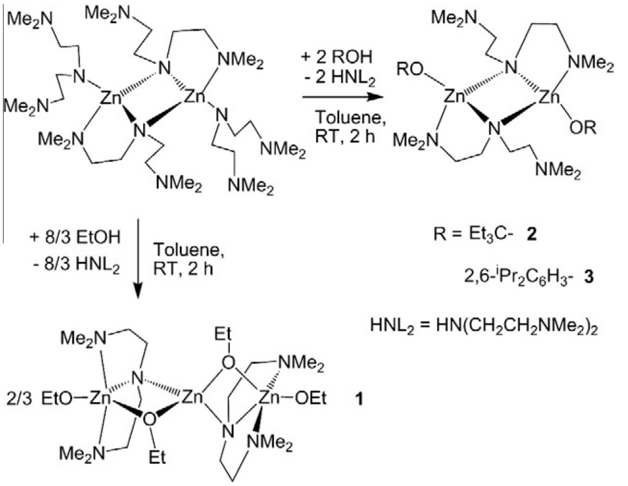
While the synthesis of compounds **2** and **3** can be understood as a ligand metathesis, the formation of **1** is unexpected. Possible reactions leading to **1** could involve the formation of the mono ethoxide intermediate [(EtO)ZnN(CH$_2$CH$_2$NMe$_2$)$_2$]$_2$ and a subsequent ligand redistribution reaction.

Compound **1** crystallizes in space group $P2_1/c$ with one molecule in the asymmetric unit. The molecule (Fig. 1) has a trinuclear $Zn_3N_2O_2$ center formed by joining two $Zn_2NO$ rings through a common Zn atom. Selected bond lengths and angles are given in Table 2. The two $Zn_2NO$ rings are slightly twisted as evidenced by the small torsion angles of N(2)–Zn(1)–O(2)–Zn(2) (3.63(5)°) and N(5)–Zn(2)–O(3)–Zn(3) (1.79(6)°). The central Zn(2) atom adopts

**Table 1**
Crystallographic data of compounds **1**–**3** and **5**.

| Chemical formula | $C_{24}H_{60}N_6O_4Zn_3$ (**1**) | $C_{30}H_{70}N_6O_2Zn_2$ (**2**) | $C_{40}H_{74}N_6O_2Zn_2$ (**3**) | $C_{20}H_{57}N_5OSi_4Zn_2$ (**5**) |
|---|---|---|---|---|
| Formula weight | 692.89 | 677.66 | 801.79 | 626.81 |
| Crystal size (mm$^3$) | 0.35 × 0.35 × 0.10 | 0.15 × 0.15 × 0.15 | 0.30 × 0.30 × 0.10 | 0.22 × 0.20 × 0.09 |
| Crystal system | monoclinic | triclinic | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1$/c | $C2/c$ |
| $a$ (Å) | 9.0047(7) | 8.8904(13) | 10.9912(12) | 17.6141(17) |
| $b$ (Å) | 15.6337(11) | 9.3616(14) | 18.248(2) | 9.0592(8) |
| $c$ (Å) | 24.1295(18) | 11.3156(17) | 11.1383(12) | 21.714(2) |
| $\alpha$ (°) | 90 | 94.612(2) | 90 | 90 |
| $\beta$ (°) | 98.2370(10) | 98.423(2) | 99.131(2) | 97.178(2) |
| $\gamma$ (°) | 90 | 94.345(2) | 90 | 90 |
| $V$ (Å$^3$) | 3361.8(4) | 924.9(2) | 2205.7(4) | 3437.8(6) |
| $Z$ | 4 | 1 | 2 | 4 |
| $T$ (°C) | −100 | −100 | −100 | −100 |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Total reflections | 38 909 | 11 160 | 25 695 | 18 913 |
| Unique reflections ($R_{\text{int}}$) | 7737(0.0278) | 4217 (0.0314) | 5072 (0.0438) | 3931 (0.0272) |
| Observed reflections | 6711 | 3717 | 4161 | 3491 |
| Completeness to theta | 27.51°, 99.9% | 27.54°, 98.7% | 27.50°, 99.9% | 27.52°, 99.6% |
| $R_1$ [$I > 2\sigma(I)$], $wR_2$ (all data)[a] | 0.0253, 0.0593 | 0.0270, 0.0728 | 0.0401, 0.0755 | 0.0267, 0.0622 |

[a] $R_1 = \sum \|F_o| - |F_c\| / \sum |F_o|$ and $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$, where $w = q/[\sigma^2(F_o^2) + (a * P)^2 + b * P + d + e * \sin(\theta)], P = (F_o^2 + 2F_c^2)/3$.



**Scheme 1.**

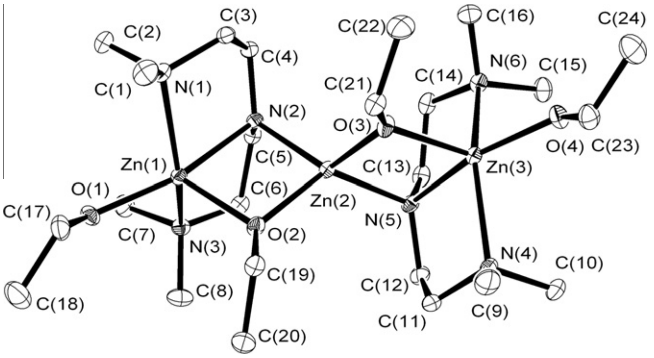


**Fig. 1.** Structure of **1** showing 20% thermal ellipsoids. Only the major disordered positions of the terminal ethoxy ligands are shown. The hydrogen atoms are omitted for clarity.

**Table 2**
Selected bond lengths (Å) and angles (°) for **1**.

| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 1.910(9) | Zn(2)–N(2) | 2.0386(13) |
| Zn(1)–O(2) | 1.9958(12) | Zn(2)–N(5) | 2.0302(14) |
| Zn(1)–N(1) | 2.2601(15) | Zn(3)–O(3) | 1.9975(12) |
| Zn(1)–N(2) | 2.1382(14) | Zn(3)–O(4) | 1.8897(16) |
| Zn(1)–N(3) | 2.2709(15) | Zn(3)–N(4) | 2.2685(15) |
| Zn(2)–O(2) | 1.9649(12) | Zn(3)–N(5) | 2.1249(15) |
| Zn(2)–O(3) | 1.9684(12) | Zn(3)–N(6) | 2.2906(15) |
| O(1)–Zn(1)–O(2) | 114.7(4) | O(3)–Zn(3)–N(4) | 103.52(5) |
| O(1)–Zn(1)–N(1) | 98.9(3) | O(3)–Zn(3)–N(5) | 85.42(5) |
| O(1)–Zn(1)–N(2) | 158.6(5) | O(3)–Zn(3)–N(6) | 101.83(5) |
| O(1)–Zn(1)–N(3) | 88.5(3) | O(4)–Zn(3)–N(4) | 99.74(8) |
| O(2)–Zn(1)–N(1) | 109.63(5) | O(4)–Zn(3)–N(5) | 155.33(8) |
| O(2)–Zn(1)–N(2) | 85.34(5) | O(4)–Zn(3)–N(6) | 87.10(7) |
| O(2)–Zn(1)–N(3) | 99.88(5) | N(4)–Zn(3)–N(5) | 80.86(6) |
| N(1)–Zn(1)–N(2) | 80.05(5) | N(4)–Zn(3)–N(6) | 146.60(6) |
| N(1)–Zn(1)–N(3) | 142.77(5) | N(5)–Zn(3)–N(6) | 79.86(6) |
| N(2)–Zn(1)–N(3) | 80.26(5) | Zn(1)–N(2)–Zn(2) | 89.56(5) |
| O(2)–Zn(2)–O(3) | 108.98(5) | Zn(1)–O(2)–Zn(2) | 95.98(5) |
| O(2)–Zn(2)–N(2) | 88.89(5) | Zn(2)–N(5)–Zn(3) | 90.06(5) |
| O(2)–Zn(2)–N(5) | 126.21(6) | Zn(2)–O(3)–Zn(3) | 95.70(5) |
| O(3)–Zn(2)–N(2) | 123.78(5) | Zn(1)–N(2)–C(4) | 111.69(10) |
| O(3)–Zn(2)–N(5) | 88.78(5) | Zn(1)–N(2)–C(5) | 110.64(10) |
| N(2)–Zn(2)–N(5) | 123.09(6) | Zn(3)–N(5)–C(12) | 111.00(11) |
| O(3)–Zn(3)–O(4) | 117.94(9) | Zn(3)–N(5)–C(13) | 110.65(11) |

a distorted tetrahedral geometry with similar N(2)–Zn(2)–O(2) (88.89(5)°) and N(5)–Zn(2)–O(3) (88.78(5)°) bond angles. Each Zn atom on the sides of the core is five-coordinate with additional ligation to the two $NMe_2$ groups of a tridentate $N(CH_2CH_2NMe_2)_2$ ligand and a terminal EtO ligand. Compounds containing a similar trinuclear $Zn_3O_4$ structure are known, including $Me_2Zn_3(OSi^iPr_3)_4$, $[(Me_3Si)_2N]_2Zn_3(OSiMe_3)_4$, $[(Me_3Si)_2N]_2Zn_3(OSiEt_3)_4$, $(C_6F_5)_2Zn_3(O\text{-}CH^iPr_2)_4$ and $(p\text{-}CF_3C_6H_4)_2Zn_3(OCH^iPr_2)_4$ [43,51].

Compounds **2** and **3** crystallize in $P\bar{1}$ and $P2_1/c$, respectively. The structures of **2** and **3** are shown in Figs. 2 and 3, respectively. Both molecules are dimeric with a crystallographically imposed inversion center. In both structures, the Zn atoms are bridged by the amide N atoms in the $N(CH_2CH_2NMe_2)_2$ ligands, one $NMe_2$ group in each $N(CH_2CH_2NMe_2)_2$ is bonded to a Zn atom forming a five-member ring, and the alkoxy or aryloxy ligand is bonded to a Zn atom at the terminal position. In the previously reported structures of $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2$ and $[EtZnN(CH_2CH_2NMe_2)_2]_2$, the bridging $N(CH_2CH_2NMe_2)_2$ ligands are bonded in a similar manner as in **2** and **3** [45].

The selected bond lengths and angles are given in Tables 3 and 4 for compounds **2** and **3**, respectively. The Zn–O bond lengths (1.8625(12) Å for **2** and 1.8852(14) Å) for **3** are comparable to the terminal Zn–O bond length in the four-coordinate Zn complex $[(2,6\text{-}F_2C_6H_3O)_2Zn(THF)]_2$ (1.869(4) Å) [16]. These bond lengths are between the terminal Zn–O bond lengths in the three-coordinate complex $[(2,6\text{-}^tBuC_6H_3O)_2Zn]_2$ (1.831(2) and 1.839(2) Å) [18] and those in the five-coordinate Zn complexes $[(F_5C_6O)_2Zn(THF)_2]_2$ (1.918(3) Å) [19] and compound **1** (1.910(9) and 1.8897(16) Å).

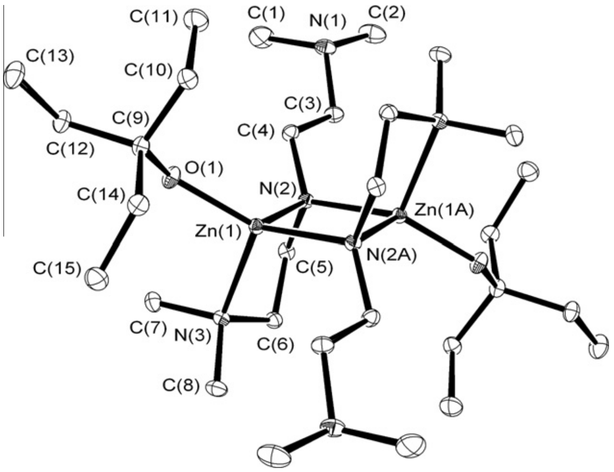


**Fig. 2.** Structure of **2** showing 20% thermal ellipsoids. The hydrogen atoms are omitted for clarity.

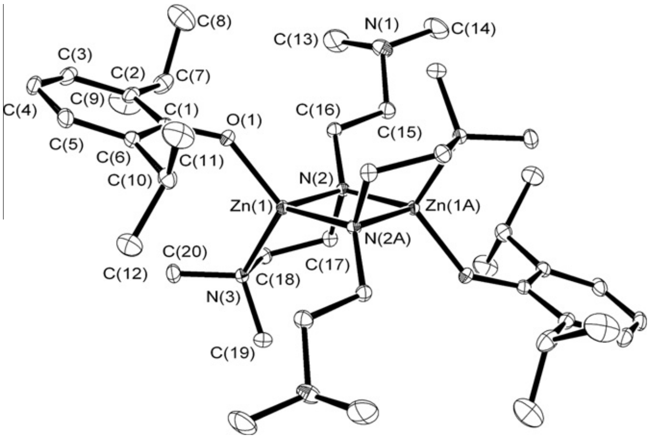


**Fig. 3.** Structure of **3** showing 20% thermal ellipsoids. The hydrogen atoms are omitted for clarity.

**Table 3**
Selected bond lengths (Å) and angles (°) for **2**.

| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 1.8625(12) | Zn(1)–N(3) | 2.1693(14) |
| Zn(1)–N(2) | 2.0931(13) | Zn(1)–N(2A)[a] | 2.0313(13) |
| O(1)–Zn(1)–N(2) | 117.16(5) | N(2)–Zn(1)–N(2A)[a] | 91.99(5) |
| O(1)–Zn(1)–N(3) | 103.90(5) | N(2)–Zn(1)–N(3) | 85.43(5) |
| O(1)–Zn(1)–N(2A)[a] | 134.85(5) | N(3)–Zn(1)–N(2A)[a] | 112.61(5) |
| Zn(1)–N(2)–Zn(1A)[a] | 88.01(5) | Zn(1)–N(3)–C(6) | 101.13(9) |
| Zn(1)–N(2)–C(5) | 107.60(10) | Zn(1)–O(1)–C(9) | 131.83(10) |

[a] Symmetry transformations used to generate equivalent atoms: $-x$, $-y+2$, $-z+2$.

**Table 4**
Selected bond lengths (Å) and angles (°) for **3**.

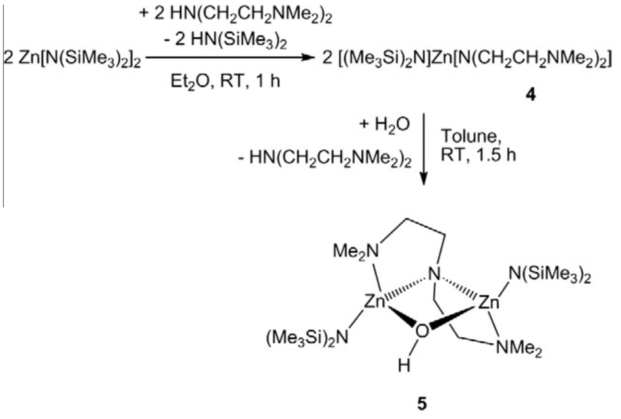
| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 1.8852(14) | Zn(1)–N(3) | 2.0920(17) |
| Zn(1)–N(2) | 1.9979(16) | Zn(1)–N(2A)[a] | 2.0824(16) |
| O(1)–Zn(1)–N(2) | 111.44(6) | Zn(1)–N(2)–Zn(1A)[a] | 86.45(6) |
| O(1)–Zn(1)–N(3) | 112.42(7) | Zn(1)–N(2)–C(16) | 113.74(12) |
| O(1)–Zn(1)–N(2A)[a] | 119.79(7) | Zn(1)–N(2)–C(17) | 103.60(12) |
| N(2)–Zn(1)–N(2A)[a] | 93.55(6) | Zn(1A)–N(2)–C(16)[a] | 122.26(13) |
| N(2)–Zn(1)–N(3) | 88.78(7) | Zn(1A)–N(2)–C(17)[a] | 113.98(13) |
| N(3)–Zn(1)–N(2A)[a] | 122.34(7) | C(16)–N(2)–C(17) | 112.40(16) |
| Zn(1)–O(1)–C(1) | 140.57(14) | | |

[a] Symmetry transformations used to generate equivalent atoms: $-x+1$, $-y$, $-z$.

The bond lengths and angles of the four-membered $Zn_2N_2$ rings in **2** and **3** are close to those in $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2$, $[EtZnN(CH_2CH_2NMe_2)_2]_2$, $[RZnNMe(CH_2)_2NMe]_2$ (R = Me or Et) and $\{RZnN[CH_2(2\text{-pyridyl})]_2\}_2$ (R = Me or $CH(SiMe_3)_2$) [41,45,52].

### 3.2. Syntheses and characterization of compounds 4 and 5

The diamide reactant in the above synthesis, $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2$, is prepared by a complete ligand exchange from $[Zn(N^{i\text{-}}Bu_2)_2]_2$ [45]. When $Zn[N(SiMe_3)_2]_2$ is reacted with 2 equiv. of $HN(CH_2CH_2NMe_2)_2$ in $Et_2O$ for 4 h at room temperature, the major product is the partial ligand exchange compound $[(Me_3Si)_2N]Zn[N(CH_2CH_2NMe_2)_2]$ (**4**). When $Zn[N(SiMe_3)_2]_2$ is reacted with 1 equiv. of $HN(CH_2CH_2NMe_2)_2$ (as shown in the first step of Scheme 2), compound **4** is isolated in 71% yield. This compound is isolated initially via recrystallization at low temperatures as a colorless, crystalline solid. It melts at room temperature, then slowly solidifies over a period of 24 h to form a glassy solid having a broad melting point. We emphasize that the room temperature $^1H$ and $^{13}C$ NMR spectra of this sample exhibit well resolved peaks showing a 1:1 molar ratio of $N(CH_2CH_2NMe_2)_2$ and $N(SiMe_3)_2$, consistent with the empirical formula $[(Me_3Si)_2N]Zn[N(CH_2CH_2NMe_2)_2]$. No resonances of $Zn[N(SiMe_3)_2]_2$, $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2$ or $HNCH_2CH_2NMe_2$ are present. In the CI mass spectrum, the most abundant Zn-containing fragments are $\{Zn[N(SiMe_3)_2]_2\text{–}Me\}^+$, $\{[(Me_3Si)_2N]Zn[N(CH_2CH_2NMe_2)_2]\text{–}CH_2NMe_2\}^+$, $\{[(Me_3Si)_2N]Zn(NH_3)_3\}^+$ and $\{Zn[N(SiMe_3)_2]\}^+$. The detection of $Zn[N(SiMe_3)_2]_2$-related ions suggests that a ligand redistribution reaction can occur, as depicted in Eq. (1), possibly during the evaporation of **4** in the mass spectrometer. Consistent with this, the peak intensities in the 380–388 mass region could be assigned as a combination of $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}^+$ ($m/e$ = 380), $\{[(Me_3Si)_2N]Zn[N(CH_2CH_2NMe_2)_2]\}^+$ ($m/e$ = 382) and $\{Zn[N(SiMe_3)_2]_2\}_2{}^+$ ($m/e$ = 384). The intensities of these ions are only ca. 2% of that of the most intense ion, $SiMe_2{}^+$. Even less in intensity (ca. 0.2%) are the ions $\{Zn[N(SiMe_3)_2]_2\}_2{}^+$ ($m/e$ = 770) and $\{[(Me_3Si)_2N]Zn\ [N(CH_2CH_2NMe_2)_2]\}_2{}^+$ ($m/e$ = 768).



**Scheme 2.**

$$2[(SiMe_3)_2N]Zn[N(CH_2CH_2NMe_2)_2] \rightleftharpoons Zn[N(SiMe_3)_2]_2 + Zn[N(CH_2CH_2NMe_2)_2]_2 \quad (1)$$

The broad melting point (49.0–62.0 °C) of the solid sample of **4** suggests it exists as a mixture, perhaps of a monomer and dimer or as a mixture of the compounds in Eq. (1). Whatever the nature of the solid, the solution NMR spectrum requires that **4** exists as a pure compound or a rapidly interconverting equilibrium mixture.

When compound **4** reacts with 1 equiv. of $H_2O$, as shown in the second step of Scheme 2, crystalline **5** is obtained in 42% yield. The elemental analysis is satisfactory. In the high mass region of its CI mass spectrum, the $[\mathbf{5}-OH]^+$ and $[\mathbf{5}-N(SiMe_3)_2]^+$ ions are detected as the major fragments. The IR spectrum of **5** exhibits a sharp OH absorption at 3709 $cm^{-1}$. Variable temperature $^1H$ NMR spectroscopy provides valuable insight into the fluxional processes of **5** (Fig. 4). At −40 °C two resonances each for the $-SiMe_3$ and $-NMe_2$ hydrogens are observed at −0.01 and −0.11 ppm and 2.29 and 2.46 ppm, respectively. This is consistent with the crystal structure. The methylenes of the amidodiamine ligand exhibit a complex pattern centered around 2.8 ppm. Definitive assignment of the hydroxyl hydrogen is complicated by the presence of a second set of resonances corresponding to an impurity (the relative integration of the peaks attributed to the impurity ranges from 5% to 8% at different temperatures). As the temperature is raised

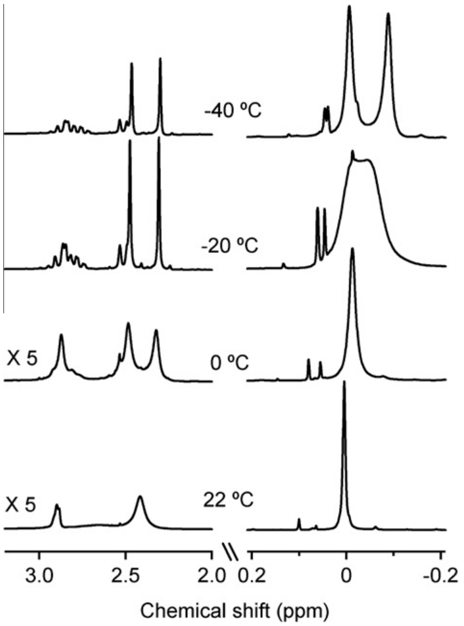
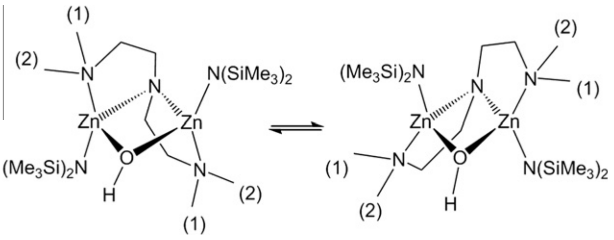


**Fig. 4.** Variable-temperature $^1H$ NMR spectra of **5** obtained in $CDCl_3$.

to −20 °C, the two resonances due to the trimethylsilyl substituents coalesce due to rotation about the Zn–N bond of the –$N(SiMe_3)_2$ ligand. At higher temperatures, both the methyl and methylene hydrogens of the amidodiamine ligand broaden, and by room temperature the methyls have coalesced into one broad resonance at 2.4 ppm. One set of methylenes has collapsed almost into the baseline while the other is clearly visible, but broadened. The changes are consistent with reversible dissociation of the –$NMe_2$ arms, coupled with rotation about the $CH_2$–$NMe_2$ bond and inversion at the nitrogen. Exchange of the –$NMe_2$ ligands between the two zinc ions could also be involved as suggested in Scheme 3.

Compound **5** crystallizes in space group *C*2/*c* with half of a molecule in the asymmetric unit and selected bond lengths and angles are given in Table 5. The OH and the amido N atom in the $N(CH_2CH_2NMe_2)_2$ bridge the two Zn atoms forming a ZnNZnO ring (Fig. 5). A crystallographic $C_2$ axis passes through the N atom and the OH group. The two $NMe_2$ groups in the $N(CH_2CH_2NMe_2)_2$ are bonded to the two Zn atoms. The $N(SiMe_3)_2$ ligands are bonded to Zn at the terminal positions. The Zn atoms and the N atoms in $N(CH_2CH_2NMe_2)_2$ are four-coordinate adopting distorted tetrahedral geometries. The geometry on the O atom was trigonal planar and that of the three-coordinate $N(SiMe_3)_2$ is nearly planar with a sum of the bond angles around the N atom being 359.3(3)°. Consistent with the sharp OH absorption in IR, no hydrogen bonding is found for OH. The bond angles in the ZnNZnO ring, e.g. Zn(1)–N(2)–Zn(1A) (90.02(8)°), Zn(1)–O(1)–Zn(1A) (95.33(7)°) and O(1)–Zn(1)–N(2) (87.33(5)°), are very close to the corresponding bond angles in the ZnNZnO rings in compound **1**.



**Scheme 3.**

**Table 5**
Selected bond lengths (Å) and angles (°) for **5**.

| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 1.9746(11) | Zn(1)–N(3) | 1.9255(14) |
| Zn(1)–N(1) | 2.1722(16) | Zn(1)–N(2) | 2.0639(14) |
| O(1)–Zn(1)–N(1) | 102.72(4) | Zn(1)–N(2)–Zn(1A)[a] | 90.02(8) |
| O(1)–Zn(1)–N(2) | 87.33(5) | Zn(1)–N(2)–C(4) | 105.42(9) |
| N(1)–Zn(1)–N(2) | 85.07(5) | Zn(1)–N(2)–C(4A)[a] | 122.47(8) |
| N(1)–Zn(1)–N(3) | 114.37(6) | C(4)–N(2)–C(4A)[a] | 110.8(2) |
| N(2)–Zn(1)–N(3) | 142.27(5) | Zn(1)–N(3)–Si(1) | 114.42(7) |
| O(1)–Zn(1)–N(3) | 116.76(5) | Zn(1)–N(3)–Si(2) | 120.96(8) |
| Zn(1)–O(1)–Zn(1A)[a] | 95.33(7) | Si(1)–N(3)–Si(2) | 123.90(8) |

[a] Symmetry transformations used to generate equivalent atoms: −*x* + 1, *y*, −*z* + 1/2.

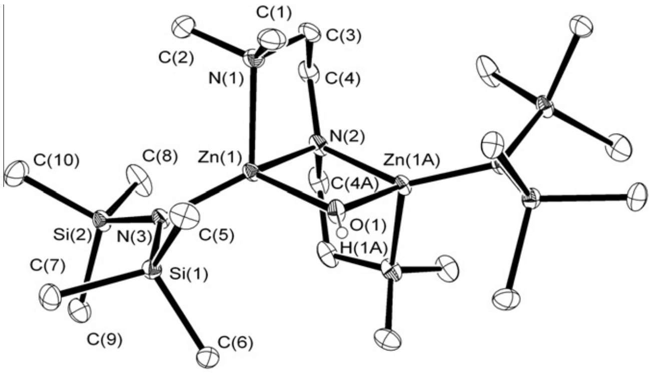
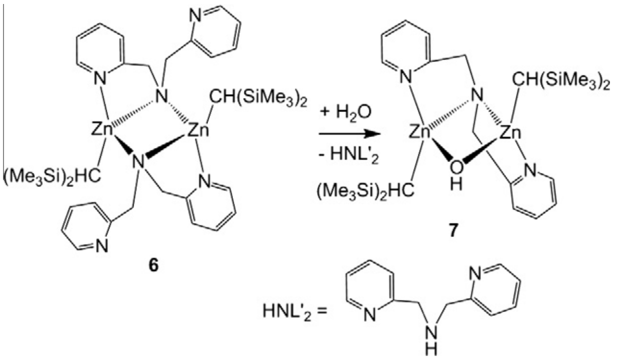


**Fig. 5.** Structure of **5** showing 20% thermal ellipsoids. The hydrogen atoms are omitted for clarity.



**Scheme 4.**

A number of hydroxyl Zn compounds have been structurally characterized, most of which are the synthetic analogs of Zn enzymes [53,54]. Other known structures include dimers $[(Me_2PhSi)_3CZn(OH)]_2$ [55] and $[(NHC)Zn(OH)(OC_6H_2\text{-}2,4,6\text{-}Me_3)]_2$ (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene) [56], a cyclic trimer $\{[\eta^2\text{-}H_2B(3\text{-tert-butylpyrazolyl})_2]Zn(OH)\}_3$ [57] and a cubane, $[(2,4,6\text{-}(CF_3)_3C_6H_2)Zn(OH)]_4$ [58]. Recently, Jaime et al. reported a compound with a structure similar to **5**, $[(SiMe_3)_2CH]_2Zn_2(OH)\{N[CH_2(2\text{-pyridyl})]_2\}$ (**7**) [52]. This compound was obtained as a minor product from the hydrolysis of the alkyl Zn amide (**6**) as illustrated in Scheme 4. In compound **7**, the tridentate bis(pyridyl)amido ligand and the hydroxyl ligand are bonded to the Zn atoms in the same manner as in compound **5**. Perhaps because of the rigidity of the pyridyl group, the ZnNZnO ring in **7** is nonplanar as evidenced by a large N–Zn–O–Zn torsion angle (13.28(7)°). The bond angles in the $Zn_2NO$ ring of **7**, Zn–N–Zn (87.90(7)°), Zn–O–Zn (91.77(7)°) and N–Zn–O (88.75(7)° and 88.58(7)°), are somewhat different from those in compound **5**.

Density functional theory (DFT) calculations conducted by Jaime et al. on the reaction between $H_2O$ and the methyl Zn analog of compound **6** were consistent with their experimental results [52]. It was found that cleavage of the amido ligand by $H_2O$ was preferred over cleavage of the alkyl ligand. The computations suggest that the lowest energy reaction path involves initial activation of $H_2O$ by the uncomplexed pyridine. It is reasonable to expect in our experiments the conversion of **4** to **5** occurs by a similar path. One might speculate that the more basic $NMe_2$ substituent in **4** should facilitate the reaction with $H_2O$, leading to the better yield of compound **5**.

## 4. Conclusions

The synthesis and structures of several alkoxo, aryloxo and hydroxo Zn complexes stabilized with the amidodiamine ligand $N(CH_2CH_2NMe_2)_2$ are reported. In the reactions of $\{Zn[N(CH_2CH_2NMe_2)_2]_2\}_2$ with alcohols in a 1:1 Zn to alcohol ratio, a trinuclear compound, **1**, is obtained from the less bulky EtOH. When using the bulky alcohols $Et_3COH$ and $2,6\text{-}^iPr_2C_6H_3OH$, stoichiometric ligand substitution takes place forming dimeric compounds **2** and **3**. In the reactions of $Zn[N(SiMe_3)_2]_2$ with $HN(CH_2CH_2NMe_2)_2$ either in a 1:1 or 1: 2 molar ratio, only the mono-substituted product $[(Me_3Si)_2N]Zn[N(CH_2CH_2NMe_2)_2]$ (**4**) is isolated. When compound **4** is reacted with $H_2O$, the cleavage of the amidodiamine ligand is preferred over the breakage of the $N(SiMe_3)_2$ leading to a hydroxo complex, $[(Me_3Si)_2N]_2Zn_2(OH)[N(CH_2CH_2NMe_2)_2]$ (**5**).

## Acknowledgements

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## Appendix A. Supplementary material

CCDC 763490, 763491, 763492 and 763493 contain the supplementary crystallographic data for compounds **1**, **2**, **3** and **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.06.029.

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