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Novel Alkyl(dialkylamido)zinc(II) Compounds: X-ray Single-Crystal Structures of $[MeZnNMe(CH_2)_3NMe_2]_2$, $[MeZnNMe(CH_2)_2NMe_2]_2$, $[EtZnNMe(CH_2)_3NMe_2]_2$, $[EtZnNMe(CH_2)_2NMe_2]_2$, $[Me_4Zn_6O_2(MeN(CH_2)_3NMe_2)_4]$, and $[Et_4Zn_6O_2(MeN(CH_2)_2NMe_2)_4]$

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The reaction of dimethyl- or diethylzinc with *N*,*N*,*N*-trimethylethylene- or propylenediamine gave a series of crystalline alkyl(dialkylamido)zinc compounds for which X-ray single-crystal structures have been determined. The four title compounds consist of dimeric molecular units, $[RZnNMe(CH_2)_nNMe_2]_2$. The same reactions in the presence of traces of moisture produced two different novel compounds whose crystal structures contain hexameric $[R_4Zn_6O_2(MeN(CH_2)_nNMe_2)_4]$ zinc units. Crystal data: $MeZnNMe(CH_2)_3NMe_2$ (**1**), orthorhombic, *Pbca*, $a = 14.578(2)$ Å, $b = 17.328(3)$ Å, $c = 15.765(3)$Å, $\beta = 90°$, $Z = 8$, $R_w = 0.1095$; $EtZn\ Me(CH_2)_3NMe_2$ (**2**), orthorhombic, *Pbca*, $a = 17.080(1)$ Å, $b = 16.062(1)$ Å, $c = 17.242(1)$ Å, $\beta = 90$, $Z = 8$, $R_w = 0.0878$; $MeZnNMe(CH_2)_2NMe_2$ (**4**), triclinic, $P\bar{1}$, $a = 7.305(1)$ Å, $b = 10.185(1)$ Å, $c = 12.307(1)$ Å, $\alpha = 82.94(1)°$, $\beta = 88.31(1)°$, $\gamma = 80.69(1)°$, $Z = 2$, $R_w = 0.1089$; $EtZnNMe(CH_2)_2NMe_2$ (**5**), triclinic, $P\bar{1}$, $a = 7.419(6)$ Å, $b = 8.317(6)$ Å, $c = 8.888(6)$Å, $\alpha = 86.13(5)°$, $\beta = 105.59(6)°$, $\gamma = 111.47(6)°$, $Z = 1$, $R_w = 0.0841$; $Me_4Zn_6O_2[MeN(CH_2)_3NMe_2]_4$ (**6**), monoclinic, $P21/n$, $a = 18.485(7)$ Å, $b = 12.585(4)$ Å, $c = 19.756(5)$ Å, $\alpha = 90°$, $\beta = 110.92(2)°$, $\gamma = 90°$, $Z = 4$, $R_w = 0.1234$; $Et_4Zn_6O_2[MeN(CH_2)_2NMe_2]_4$ (**7**), monoclinic, $I2$, $a = 11.387(1)$ Å, $b = 15.547(1)$ Å, $c = 12.320(1)$ Å, $\beta = 90°$, $Z = 2$, $R_w = 0.0906$.

Introduction

Bis(diethylamido)zinc was first prepared by Frankland[1] in 1856, and many compounds containing Zn−N bonds have since been reported.[2] Alkyl−dialkylamido compounds of zinc generaly adopt dimeric structures in the solid state[3−6] whereas the bis(dialkyamido)zinc compounds are usually polymeric.[4−8] There are many compounds with bulky groups such as $Zn[N(Si(CH_3)_3]_2$[9] and $Zn[N(C(CH_3)_3Si(CH_3)_3]_2$[10] which are monomeric. Recently Reese et al.[11−15] have detailed the synthesis and chracterization of a series of bis(alkylamido)zinc compounds some of which have been investigated as precursors for the nitrogen-doping of II/VI materials in MOCVD. We have, in the course of related work, investigated the chemistry of several novel zinc alkylamides, some of which are described in this paper. These compounds may be useful zinc precursors with p-doping properties for ZnSe layers.

Experimental Section

Chemicals. Butyllithium, diethylzinc, dimethylamine, diethylamine, zinc chloride, *N*,*N*,*N*-trimethylpropylenediamine and *N*,*N*,*N*-trimethylethylenediamine were purchased from Aldrich Chemical Co. Ltd. Dimethylzinc was from Epichem Ltd. and solvents were obtained from BDH and were dried and degassed before use.

Physical Measurements. NMR spectra were recorded using a Bruker AM250 pulsed Fourier transform instrument. Melting points were measured in sealed tubes with an electrothermal melting point apparatus and are uncorrected. Microanalyses were carried out by the University College London service.

Crystallography. The structures of compounds **1**, **2**, **and 4−7** were determined by single-crystal methods. Measurements were made on samples mounted in glass capillaries. The intensity data were collected with a CAD4 diffractometer in $\omega/2\theta$ scan mode with graphite-monochromated Mo Kα radiation as described previously.[16] Absorption corrections were made for compounds **1**, **2**, **4,** and **5** with the ψ-scan method.[17] The unit cell parameters were determined by a least-squares refinement on diffractometer angles for automatically centered reflections. The structures were solved by the heavy-atom method using the SHELXS program package[18] and then refined anisotropically (non-hydrogen atoms) by full-matrix least-squares on F^2, using the SHELX-

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Table 1. Crystal Data and Structure Refinement

	1	**2**	**4**	**5**	**6**	**7**
chem formula	$C_{14}H_{36}N_4Zn_2$	$C_{16}H_{40}N_4Zn_2$	$C_{12}H_{32}N_4Zn_2$	$C_{14}H_{36}N_4Zn_2$	$C_{28}H_{72}N_8O_2Zn_6$	$C_{28}H_{72}N_8O_2Zn_6$
fw	391.21	419.26	363.16	391.21	945.16	945.16
T, °C	20	20	20	20	20	20
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
cryst syst	orthorhombic	orthorhombic	triclinic	triclinic	monoclinic	monoclinic
space group	$Pbca$	$Pbca$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$I2$
a, Å	14.578(2)	17.080(1)	7.305(1)	7.419(6)	18.485(7)	11.387(1)
b, Å	17.328(3)	16.062(1)	10.185(1)	8.317(6)	12.585(4)	15.547(1)
c, Å	15.765(3)	17.242(1)	12.307(1)	8.888(6)	19.756(5)	12.320(1)
α, deg	90	90	82.94(1)	86.13(5)	90	90
β, deg	90	90	88.31(1)	105.59(6)	110.92(2)	90.18(2)
γ, deg	90	90	80.69(1)	111.47(6)	90	90
V, Å^3	3982.4(12)	4435.7(5)	896.7(2)	491.3(6)	4293(2)	2181(3)
Z	8	8	2	1	4	2
D_{calc}, g cm^{-3}	1.305	1.256	1.345	1.322	1.462	1.439
$F(000)$	1664	1792	384	208	1968	984
μ, cm^{-1}	2.407	2.166	2.667	2.439	3.331	3.278
data restraints, params	3492, 0, 203	3905, 0, 224	3147, 0, 184	1720, 0, 102	7525, 0, 441	2002, 1, 222
final R^a	0.0501	0.0388	0.0421	0.0307	0.0533	0.0370
final R_wb	0. 1095	0.0878	0. 1089	0.0841	0.1234	0.0906

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w{}^b = [\sum w(|F_o| - |F_c|)^2/w(F_o)^2]^{1/2}$.

Table 2. Analysis of Bis(alkylamido)zinc and Alkyl(alkylamido)zinc

compd	yield (%)	melting pt (°C)	found (%)			formula	calcd (%)		
			C	H	N		C	H	N
$MeZnMeN(CH_2)_3NMe_2$ (**1**)	59	77	41.8	8.9	13.8	$C_7H_{18}N_2Zn$	43.0	9.3	14.3
$EtZnMeN(CH_2)_3NMe_2$ (**2**)	47	88−90	44.0	9.3	12.9	$C_8H_{20}N_2Zn$	45.8	9.6	13.4
$Zn(MeN(CH_2)_3NMe_2)_2$ (**3**)	79	87	47.2	9.9	17.1	$C_{12}H_{30}N_4Zn$	48.7	10.2	18.9
$MeZnMeN(CH_2)_2NMe_2$ (**4**)	83	110	38.4	8.4	14.8	$C_6H_{16}N_2Zn$	39.7	8.9	15.3
$EtZnMeN(CH_2)_2NMe_2$ (**5**)	87	85	41.3	8.8	13.8	$C_7H_{22}N_2Zn$	43.0	9.3	14.3
$Me_4Zn_6O_2[MeN(CH_2)_3NMe_2]_4$ (**6**)	43	87−89	36.0	7.6	12.0	$C_{28}H_{72}N_8O_2Zn_6$	35.6	7.7	11.9
$Et_4Zn_6O_2[MeN(CH_2)_2NMe_2]_4$ (**7**)	45	91−92	35.9	7.5	11.6	$C_{28}H_{72}N_8O_2Zn_6$	35.6	7.7	11.9

93 program.[19] All hydrogen atoms were calculated geometrically (riding model) using the AFIX command of the SHELXL-93 program. The programs SNOOPI[20a] and ORTEP-3[20b] were used for drawing molecular structures. Crystal data and details of the intensity measurements and refinements are given in Table 1.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

Synthesis. All reactions were performed under an inert atmosphere using standard Schlenk techniques. Microanalyses, yields, and melting points are given in Table 2.

Methyl(*N,N,N*-trimethylpropylenediamido)zinc (1). A mixture of dimethylzinc (3.8 g, 39.8 mmol) and *N,N,N*-trimethylpropylenediamine (4.8 g, 41.3 mmol) in toluene (30 cm^3) was stirred at 60−70 °C for 3 h. The solvent was evaporated, and the white product was redissolved in hexane to recrystallize. Transparent needles identified as methyl(*N,N,N*-trimethylpropylenediamido)zinc were obtained.

NMR data: ^{1}H NMR ([$^2H_6$]C_6H_6), 250 MHz) δ (ppm) −0.45, −0.43 [3H, s, MeZn], 1.65 [2H, quintet, $CH_2\mathit{CH}_2CH_2$], 1.96, 2.03 [6H, s, NMe_2], 1.19 [2H, t, NCH_2], 2.86, 2.92 [3H, s, NMe], 3.12, 3.19 [2H, t, NCH_2]; $^{13}C\{^1H\}$ NMR ([$^2H_6$]C_6H_6), 62.9 MHz) δ (ppm) −15.86, −13.22 [CH_3Zn], 24.57, 25.67 [CH_3CH_2Zn], 37.65 [$CH_2\mathit{CH}_2CH_2$], 46.34, 46.77 [NMe_2], 48.78, 49.54 [NCH_2], 61.71 [NMe], 63.85, 64.27 [NCH_2].

Ethyl(*N,N,N*-trimethylpropylenediamido)zinc (2). Diethylzinc (3.5 g, 28.4 mmol) and *N,N,N*-trimethylpropylenediamine (3.4 g, 29.3 mmol) in toluene (30 cm^3) were stirred at 70 °C for 3 h. The solvent was evaporated completely, and the product was recrystallized from hexane to give transparent crystals of ethyl(*N,N,N*-trimethylpropylenediamido)zinc.

NMR data: ^{1}H NMR ([$^2H_6$]C_6H_6), 250 MHz) δ (ppm) 0.53 [2H, q, q, $^3J_{H-H}$ = 8.2 CH_2Zn], 1.79, 1.90 [3H, t, $^3J_{H-H}$ = 8.2 CH_3CH_2Zn], 1.43, 1.67 [2H, broad, $CH_2\mathit{CH}_2CH_2$], 1.99, 2.09 [6H, s, NMe_2], 2.21 [2H, broad, NCH_2], 2.86, 2.96 [3H, s, NMe], 3.15 [2H, t, NCH_2]; $^{13}C\{^1H\}$ NMR ([$^2H_6$]C_6H_6), 62.9 MHz) δ (ppm) −1.96, 0.20 [CH_2Zn], 15.68 [CH_3CH_2Zn], 24.34, 25.66 [$CH_2\mathit{CH}_2CH_2$], 46.66, 48.75 [NMe_2], 61.96, 64.39 [NCH_2], 45.02, 47.82 [NCH_2], 61.19 [NMe].

Bis(*N,N,N*-trimethylpropylenediamido)zinc (3). A mixture of butyllithium (0.87 g, 13.5 mmol) and *N,N,N*-trimethylpropylenediamine (1.58 g, 13.5 mmol), in ether, was reacted at −196 °C under nitrogen and allowed to warm slowly at room temperature while stirring. After 0.5 h of stirring at room temperature zinc chloride (0.92 g, 6.7 mmol) was added into the mixture. Lithium chloride was removed by filtration to give a clear solution of bis(*N,N,N*-trimethylpropylenediamido)zinc. After complete evaporation of the solvent the product appeared as viscous nonvolatile solid.

NMR data: ^{1}H NMR ([$^2H_6$]C_6H_6), 250 MHz) δ (ppm) 1.50 [2H, quintet, $CH_2\mathit{CH}_2CH_2$], 2.17 [6H, s, NMe_2], 2.25 [2H, t, NCH_2], 2.28 [3H, s, NMe], 3.01 [2H, broad, NCH_2]; $^{13}C\{^1H\}$ NMR ([$^2H_6$]C_6H_6), 62.9 MHz) δ (ppm) 28.46 [$CH_2\mathit{CH}_2CH_2$], 46.39 [NMe_2], 59.49 [NCH_2], 46.67 [NCH_2], 51.87 [NMe].

Methyl(*N,N,N*-trimethylethylenediamido)zinc (4). Methyl(*N,N,N*-trimethylethylenediamido)zinc was prepared by the literature method.[4] The white product was recrystallized from hot hexane to give transparent crystals of methyl(*N,N,N*-trimethylethylenediamido)zinc.

NMR data: ^{1}H NMR ([$^2H_6$]C_6H_6), 250 MHz) δ (ppm) −0.52 (strong), −0.45 (weak) [3H, s, CH_3Zn], 2.76 [3H, s, ZnN*Me*], 2.86 [2H, broad, $ZnNMe\mathit{CH}_2$], 2.38 [2H, broad, $Me_2N\mathit{CH}_2$], 1.96 [6H, s, NMe_2]; $^{13}C\{^1H\}$ NMR ([$^2H_6$]C_6H_6), 62.9 MHz) δ (ppm) −19.80, −14.32 [CH_3Zn], 56.36, 55.74 [ZnN*Me*], 62.30, 62.31 [$ZnNMe\mathit{CH}_2$], 46.26 [$Me_2N\mathit{CH}_2$], 45.07, 45.00 [NMe_2].

Ethyl(*N,N,N*-trimethylethylenediamido)zinc (5). A mixture of diethylzinc (2.67 g, 21.6 mmol) and *N,N,N*-trimethylethylenediamine (2.21 g, 21.6 mmol) in toluene (30 cm^3) was stirred at 40−60 °C for 5 h under nitrogen. The solvent was evaporated to dryness, and the solid product was recrystallized from hot hexane to give transparent crystals of ethyl(*N,N,N*-trimethylethylenediamido)zinc.

NMR data: ^{1}H NMR ([$^2H_6$]C_6H_6), 250 MHz) δ (ppm) 0.45 [2H, multiplet, CH_2Zn], 1.76, 1.69 [3H, t, $^3J_{H-H}$ = 8.2 CH_3CH_2Zn], 2.68 [3H, s, ZnN*Me*], 2.84 [2H, broad, $ZnNMe\mathit{CH}_2$], 2.24 [2H, broad,

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Me$_2$N*CH*$_2$], 1.98 [6H, s, NMe$_2$]; ^{13}C{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz) δ (ppm) −1.23 [CH$_2$Zn], 15.68 [*CH*$_3$CH$_2$Zn], 50.85 [ZnN*Me*], 60.15 [ZnNMe*CH*$_2$], 46.23 [Me$_2$N*CH*$_2$], 37.51 [NMe$_2$].

Preparation of Me$_4$Zn$_6$O$_2$[NMe(CH$_2$)$_3$NMe$_2$]$_4$ (6). This compound was first prepared accidentally by the reaction of dimethylzinc and *N*,*N*,*N*-trimethylpropylenediamine in toluene containing traces of water. The expected product **4** was later prepared by using dry toluene, and **6** was subsequently reproducibly prepared by the reaction of dimethylzinc (4.64 g, 48.6 mmol) and *N*,*N*,*N*-trimethylpropylenediamine (5.68g, 48.6 mmol) in toluene (30 cm^3) containing 0.3 g, 16.5 mmol, of water and stirred at 70 °C for 2 h. The solvent was evaporated completely, and the solid was crystallized from hot toluene. The product was identified as Me$_4$Zn$_6$O$_2$[NMe(CH2)$_3$NMe]$_4$.

NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz) δ (ppm) −0.42, −0.45 [3H, s, CH$_3$Zn], 1.44, 1.65 [2H, broad, quintet, CH$_2$*CH*$_2$CH$_2$], 1.95, 2.02 [6H, s, NMe$_2$], 2.20, 2.26 [2H, t, broad, NCH$_2$], 2.86, 2.93 [3H, s, NMe], 3.12, 3.20 [2H, t, NCH$_2$]; ^{13}C{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz) δ (ppm) −17.78, −15.86 [CH$_3$Zn], 24.48, 25.62 [CH$_2$*CH*$_2$CH$_2$], 46.33, 48.76 [NMe$_2$], 44.73, 47.79 [NCH$_2$], 61.05 [NCH$_2$], 61.88, 64.24 [NMe].

Preparation of Et$_4$Zn$_6$O$_2$[NMe(CH$_2$)$_2$NMe$_2$]$_4$ (7). Preparation was as for compound **6** using diethylzinc and *N*,*N*,*N*-trimethylethylenediamine and recrystallized from hot hexane.

NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz) δ (ppm) 0.44 [8H, q(d), $^3J_{\mathrm{H-H}} = 8.2$ CH$_2$Zn], 1.7 [12H, t, $^3J_{\mathrm{H-H}} = 8.2$ *CH*$_3$CH$_2$Zn], 2.79-[12H, s, ZnN*Me*], 2.88 [8H, broad, ZnNMe*CH*$_2$], 2.39 [2H, broad, Me$_2$N*CH*$_2$], 2.01 [6H, s, NMe$_2$]; ^{13}C{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz) δ (ppm) −3.23 [CH$_2$Zn], 15.67 [*CH*$_3$CH$_2$Zn], 46.39 [ZnN*Me*], 62.50 [ZnNMe*CH*$_2$], 56.60 [Me$_2$N*CH*$_2$], 45.63 [NMe$_2$].

Results and Discussion

The compounds are all air-sensitive crystalline solids soluble in organic solvents which can easily be recrystallized from hexane or toluene. In sealed tubes, under nitrogen, after few days at room temperature they change color from white to yellow but can be stored under nitrogen at low temperature (0 °C) for several months. X-ray crystal structures for several compounds have been determined from single crystals. The alkyl−*N*,*N*,*N*-trimethylpropylenediamido and alkyl−*N*,*N*,*N*-trimethylethylenediamido compounds are dimers [(RZnNMe(CH$_2$)*n*NMe$_2$)]$_2$ **(1**, **2**, **4**, **5)** whereas the oxo-centered compounds **6** and **7** are hexamers (R$_4$Zn$_6$O$_2$[NMe(CH$_2$)$_n$NMe$_2$]$_4$). There is no evidence for any bis(amido) products from the reactions of these amines with alkyls, an observation which is common for such reactions.[21] Microanalyses, yields, and melting points are given in Table 2.

Spectroscopic Studies. The solution ^{1}H NMR spectra of the crystalline compounds **1**, **2**, **4**, and **5** showed almost twice the number of signals expected despite their analytical purity, indicating the presence of more than one species in solution. Typical results, for methyl(*N*,*N*,*N*-trimethylpropylenediamido)zinc **(1)**, show the ^{1}H NMR spectrum to contain two singlets for the ZnCH$_3$ protons, two for N(CH$_3$)$_2$, two for NCH$_3$, and two multiplets for each of the methylene protons. The same sample, after 50% dilution, showed a spectrum with the corresponding change in intensities of these two sets of signals indicating a mixture of dimer and monomer. The signals which gain intensity on dilution belong to the monomer, and those which lose intensity correspond to the dimer. In compound **2** ZnCH$_2$ protons show two different sets of quartets. The quartet at lower field of enhanced intensity on dilution belongs to the monomer, and the second quartet, at higher field, which splits further to give a 14-line signal corresponds to the dimer. Two clear triplets next to each other at 1.85 ppm are for the methyl protons (Experimental Section). Similarly NMe$_2$ and NMe both show a double set of the signals. The ^{13}C NMR spectra showed also twice the number of signals than expected for all four compounds again confirming a dimer/monomer mixture in solution (see Experimental Section).

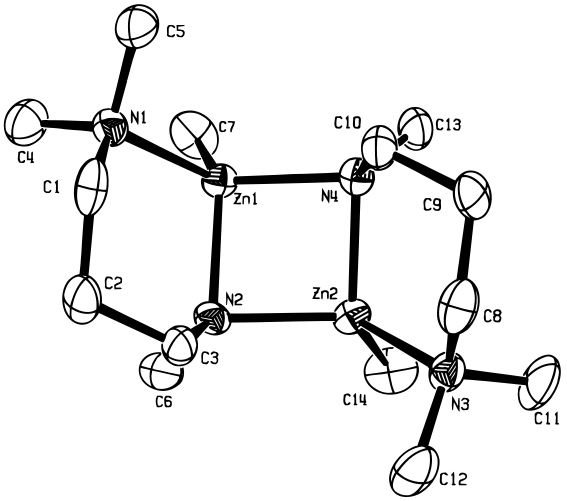

Figure 1. Structure of [MeZnNMe(CH$_2$)$_3$NMe]$_2$.

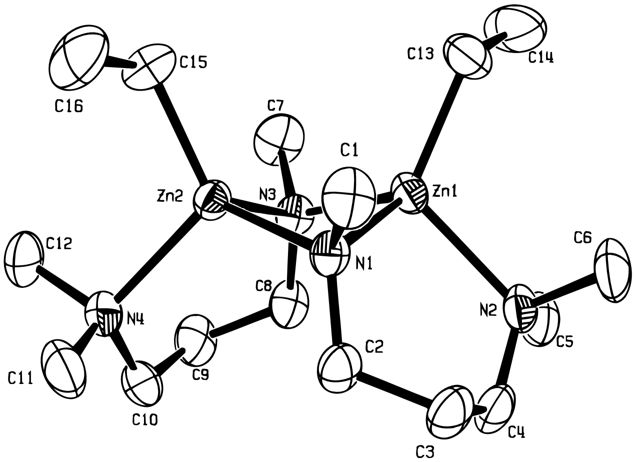

Figure 2. Structure of [EtZnNMe(CH$_2$)$_3$NMe]$_2$.

The ^{1}H spectrum for compound **6** gave two sets of multiplets for the methyl and methylene groups again showing the presence of a dimer and monomer mixture, but compound **7** gave a clear spectrum for a single species. Further splitting of the quartet for the ZnCH$_2$ protons indicates that these protons are nonequivalent and that they couple with each other and to the neighboring methyl protons. The ^{13}C NMR spectrum for compound **6** also showed two types of signals whereas only a seven-line spectrum was observed for compound **7** as expected for a single species.

Crystal Structures. The structures of methyl(*N*,*N*,*N*-trimethylpropylenediamido)zinc **(1)**, ethyl(*N*,*N*,*N*-trimethylpropylenediamido)zinc **(2)**, methyl(*N*,*N*,*N*-trimethylethylenediamido)zinc **(4),** and ethyl(*N*,*N*,*N*-trimethylethylenediamido)zinc **(5)** are based on dimers [RZnNMe(CH$_2$)$_n$NMe$_2$]$_2$, where each zinc atom is coordinated to three nitrogen and one carbon atoms. The coordination at the metal center is close to tetrahedral. The amide nitrogen (NMe) bridges the two zinc atoms whereas the amine nitrogen (NMe$_2$) bonds to one zinc. The molecular structure of all four compounds are shown in Figures 1−4, and selected bond lengths and angles are given in Table 3.

The structures of the dimeric compounds [MeZnNMe(CH$_2$)$_2$-NMe]$_2$ **(4)** and [MeZnNMe(CH$_2$)$_2$NMe]$_2$ **(5)** are centrosymmetric whereas the molecules in [MeZnNMe(CH$_2$)$_3$NMe]$_2$ **(1)** and [MeZnNMe(CH$_2$)$_3$NMe]$_2$ **(2)** occupy general positions. The difference between the two types is that one contains propylenediamine and the other ethylenediamine, giving rise to structures with six-membered and five-membered rings, respec-

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(21) Malik, M. A.; Motevalli, M.; O'Brien, P. *Polyhedron* **1997**, *16*, 3593.

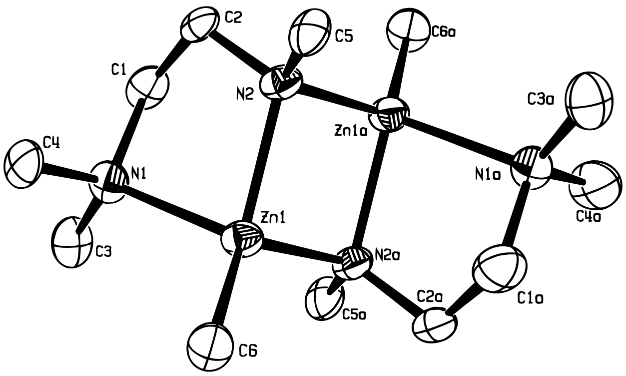

Figure 3. Structure of [MeZnNMe(CH$_2$)$_2$NMe]$_2$.

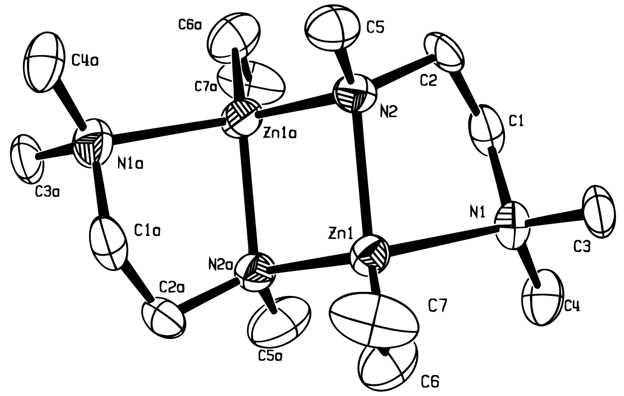

Figure 4. Structure of [EtZnNMe(CH$_2$)$_2$NMe]$_2$.

tively. In our related structural studies of ethylzinc selenocarbamates[22] the ethyl groups are often disordered and do not allow the molecule to acquire a center of symmetry, but in this case both **4** and **5** possess centers of symmetry.

In all four structures two different Zn−N bond distance are observed. The Zn−N bond distance for the bridging amido nitrogen is 2.05(1) Å (average) while the distance for nonbridged nitrogen is 2.20(1) Å (average). A similar difference was noted in the closely related structure of [HZnN(Me)(CH$_2$)$_3$NMe$_2$]$_2$ in which the Zn−N distance for bridging amido nitrogen was 2.06(1) Å and 2.19(1) Å for the other nitrogen.[23] The Zn−N(amido) bond distance (2.05(1) Å) is close to that observed in [EtZn(NHPh)THF]$_3$ (2.07(2), 2.03(2), and 2.06(2) Å),[24] (Me$_3$SiCH$_2$ZnNHDipp)$_2$ (2.07(4), (2.01(4) Å),[24] [EtZn(THF)NHMes]$_2$ (2.07(5) Å),[24] and [EtZnNH(^{t}Bu)]$_3$ (2.01(7), 2.04(8), 2.03(8) Å)[24] and considerably larger than those observed in ((trimethylsilyl)amido)(1-methyl-2-((*N-tert*-butylamino)methyl)benzimidazole)zinc(II) (1.874(4) and 1.887(4) Å),[25] Zn$_2$[N(SiMe$_3$)$_2$]{S[2,4,6-(CF)$_3$C$_6$H$_2$]}$_3$ (1.993(7) Å),[26] Zn$_3$[N(SiMe$_3$)$_2$]{S[2,4,6-(iPr)$_3$C$_6$H$_2$]}$_4$ (1.863(7) Å),[26] Zn$_2$[N(SiMe$_3$)$_2$]2{O[2,4,6-(CF)$_3$C$_6$H$_2$]}$_2$ (1.854(6), (1.856(6) Å),[26] [Na(12-Krone-4)2-[Zn[N{(Si(CH$_3$)$_3$}$_2$]$_3$] (1.957(7) (average)),[27] Zn{N(SiMePh$_2$)$_2$}$_2$ (1.849(3) Å),[28] [Et$_2$Zn$_4$(NHDipp)$_4$(OEt)$_2$ (1.95(4), 1.96(4) Å),[24] Zn[{C(CH$_3$)$_3$(Si(CH$_3$)$_3$}$_2$]$_2$ (1.823(8), 1.812(8) Å),[10] and Zn-[N{(Si(CH$_3$)$_3$}$_2$]$_2$ (1.82 Å)[9] as determined by gas electron differaction.

The Zn−N (nonbridged) distance (2.20(1) Å (average)) is close to that observed in [(Et$_2$NCO$_2$)$_2$Zn(Me$_2$NCH$_2$)$_2$] (2.179(6), 2.208(9) Å),[29] [(Me$_2$NCH$_2$)$_2$Zn(O$_2$CNEt$_2$)$_2$] (2.208(9) Å),[29] and [MeZnSBu^t•C$_6$H$_{15}$N$_3$]$_2$ (2.22 Å)[34] but is longer than those of [Me^{i}PrNCS$_2$)$_2$Zn(Me$_2$N(CH$_2$)$_2$NMe$_2$)]$_2$ (2.137(5) Å),[30] lithium (bis(trimethylsilyl)amino)bis((trimethylsilyl)methyl)zincate•-TMTA (2.13(3) Å),[31] benzimidazole (2.067(4) Å),[24] [C$_5$H$_5$NZn$_2$Me$_2$(O$_2$CNEt$_2$)$_3$] (2.057(6) Å),[29] C$_5$H$_5$NZn(S$_2$CNMe$_2$)$_2$ (2.079(4) Å),[32] [(Me^{i}PrNCS$_2$)$_2$ZnNC$_5$H$_5$] (2.069(2) Å)[30] and [(CNS)Zn-S$_2$CNMe$_2$)]$^-$ (1.954(9) Å),[33] and [MeZnSBu^t•C$_5$H$_5$N]$_2$ (2.156 Å)[34] and is substantially shorter than those in Me$_2$N(CH$_2$)$_3$Zn (2.307(4) Å)[35] and other adducts, such as Me$_2$Zn[(CH$_2$NMe)$_3$]$_2$ (2.41 Å),[36,37] Me$_2$Zn[Me$_2$N(CH$_2$)$_2$NMe$_2$] (2.27 Å),[38] [Me$_2$N-(CH$_2$)$_3$]$_2$Zn (2.31 Å),[35] and (Me$_3$CCH$_2$)$_2$Zn[Me$_2$N(CH$_2$)$_2$NMe$_2$] (2.41 Å).[37] The Zn−C (2.01 Å average) bond length is slightly longer than in typical alkyls (1.89−1.99 Å). Selected bond lengths and angles are given in Table 3.

The structures of compounds **6** and **7** are based on R$_4$Zn$_6$O$_2$[NMe(CH$_2$)$_n$NMe]$_4$ units (Figures 5 and 6). Each zinc is four coordinate with a distorted tetrahedral geometry. Four of the six zinc atoms are bonded to one carbon, one oxygen, and two nitrogen atoms whereas the other two are attached to two nitrogen and two oxygen atoms. The structure of compound **6** consist of four six- and five four-membered rings fused together whereas the structure of compound **7** is based on four five-membered and five four-membered rings. The nitrogen and oxygen atoms are four coordinate in both structures. Oxygen uses both lone pairs of electrons in a coordination mode similar to that in the methylzinc methoxide tetramer[39] but different from those in methylzinc acetoximate tetramer[40] and alkylamide {Zn(μ-OCEt$_3$)[N(SiMe$_3$)$_2$]},[41] in which the nitrogen and oxygen are three coordinate. The molecule Me$_4$Zn$_6$O$_2$[NMe(CH$_2$)$_3$NMe]$_4$ **(6)** occupies a general position whereas for Et$_4$Zn$_6$O$_2$[NMe(CH$_2$)$_2$NMe]$_4$ **(7)** the molecule has a 2-fold rotational axis. Selected bond lengths and angles are given in Table 3.

In compounds **6** and **7** bond lengths of Zn−O are in the range of 1.99−2.05(1) Å and the Zn−N bond distances are between 1.99 and 2.22(1) Å. The four zinc atoms which are linked to one carbon other than a nitrogen and oxygen give slightly smaller Zn−O bond distances than the remaining two which are linked only to an oxygen and nitrogen, but this order is reverse for Zn−N bonds. The bridging Zn−N bond is always shorter than that of the four outer zinc atoms (nonbridging) in compounds **1**,**2**, **4**, and **5**. The Zn−O bond distances are similar to those in [Zn$_2$Et(OCHMeCH$_2$OMe)$_3$]$_2$ (1.95(1)−2.03(1) Å),[42]

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Table 3. Selected Bond Lengths (Å) and Angles (deg)

		Compound **1**			
Zn(1)−C(7)	1.982(7)	Zn(1)−N(1)	2.226(5)	Zn(2)−N(4)	2.052(5)
Zn(1)−N(2)	1.044(5)	Zn(2)−C(14)	1.976(7)	Zn(2)−N(3)	2.203(5)
Zn(1)−N(4)	2.073(5)	Zn(2)−N(2)	2.049(5)		
C(7)−Zn(1)−N(2)	125.5(3)	N(2)−Zn(1)−N(1)	96.4(2)	N(2)−Zn(2)−N(4)	89.9(2)
C(7)−Zn(1)−N(4)	117.4(3)	N(4)−Zn(1)−N(1)	116.3(2)	C(14)−Zn(2)−N(3)	107.7(3)
N(2)−Zn(1)−N(4)	89.4(2)	C(14)−Zn(2)−N(2)	117.4(3)	N(2)−Zn(2)−N(3)	115.7(2)
C(7)−Zn(1)−N(1)	109.6(3)	C(14)−Zn(2)−N(4)	126.4(3)	N(4)−Zn(2)−N(3)	98.3(2)
		Compound **2**			
Zn(1)−C(13)	2.024(4)	Zn(1)−N(2)	2.208(3)	Zn(2)−N(3)	2.059(2)
Zn(1)−N(1)	2.049(2)	Zn(2)−C(15)	2.010(3)	Zn(2)−N(4)	2.199(3)
Zn(1)−N(3)	2.055(2)	Zn(2)−N(1)	2.056(2)		
C(13)−Zn(1)−N(1)	122.4(2)	N(3)−Zn(1)−N(2)	113.43(10)	N(1)−Zn(2)−N(4)	113.40(10)
C(13)−Zn(1)−N(3)	117.2(2)	C(15)−Zn(2)−N(1)	117.25(13)	N(3)−Zn(2)−N(4)	97.75(11)
N(1)−Zn(1)−N(3)	90.19(9)	C(15)−Zn(2)−N(3)	122.55(13)	Zn(1)−N(1)−Zn(2)	83.11(9)
C(13)−Zn(1)−N(2)	112.70(14)	N(1)−Zn(2)−N(3)	89.87(9)	Zn(1)−N(3)−Zn(2)	82.90(9)
N(1)−Zn(1)−N(2)	98.01(10)	C(15)−Zn(2)−N(4)	112.92(14)		
		Compound **4**			
Zn(1)−C(6)	1.978(4)	Zn(2)−C(12)	1.991(4)	N(2)−Zn(1)#1	2.067(3)
Zn(1)−N(2)	2.063(3)	Zn(2)−N(4)	2.066(3)	N(4)−Zn(2)#2	2.079(3)
Zn(1)−N(2)#1	2.067(3)	Zn(2)−N(4)#2	2.079(3)		
Zn(1)−N(1)	2.192(3)	Zn(2)−N(3)	2.200(3)		
C(6)−Zn(1)−N(2)	129.3(2)	N(2)−Zn(1)−N(1)	83.62(11)	N(4)−Zn(2)−N(4)#2	91.15(10)
C(6)−Zn(1)−N(2)#1	121.9(2)	N(2)#1−Zn(1)−N(1)	109.88(11)	C(12)−Zn(2)−N(3)	116.4(2)
N(2)−Zn(1)−N(2)#1	91.20(10)	C(12)−Zn(2)−N(4)	129.7(2)	N(4)−Zn(2)−N(3)	83.92(11)
C(6)−Zn(1)−N(1)	113.8(2)	C(12)−Zn(2)−N(4)#2	120.6(2)	N(4)#2−Zn(2)−N(3)	107.80(11)
		Compound **5**			
Zn(1)−C(6)	1.989(3)	Zn(1)−N(2)#1	2.071(3)	N(2)−Zn(1)#1	2.071(3)
Zn(1)−N(2)	2.069(3)	Zn(1)−N(1)	2.196(3)		
C(6)−Zn(1)−N(2)	130.87(14)	C(6)−Zn(1)−N(1)	113.1(2)	Zn(1)−N(2)−Zn(1)#1	88.78(10)
C(6)−Zn(1)−N(2)#1	121.72(14)	N(2)−Zn(1)−N(1)	83.71(12)		
N(2)−Zn(1)−N(2)#1	91.22(10)	N(2)#1−Zn(1)−N(1)	109.25(11)		
		Compound **6**			
Zn(1)−O(1)	1.988(4)	Zn(3)−C(14)	1.971(9)	Zn(5)−N(6)	1.994(6)
Zn(1)−C(1)	1.986(10)	Zn(3)−O(2)	1.996(5)	Zn(5)−N(7)	2.000(5)
Zn(1)−N(2)	2.080(6)	Zn(3)−N(3)	2.091(6)	Zn(5)−O(1)	2.042(4)
Zn(1)−N(1)	2.252(8)	Zn(3)−N(4)	2.244(7)	Zn(5)−O(2)	2.049(5)
Zn(2)−N(2)	1.995(6)	Zn(4)−C(15)	1.989(8)	Zn(6)−C(28)	1.977(8)
Zn(2)−N(3)	1.993(6)	Zn(4)−O(2)	2.016(5)	Zn(6)−O(1)	2.005(4)
Zn(2)−O(1)	2.038(5)	Zn(4)−N(6)	2.087(7)	Zn(6)−N(7)	2.094(6)
Zn(2)−O(2)	2.040(5)	Zn(4)−N(5)	2.228(7)	Zn(6)−N(8)	2.219(7)
O(1)−Zn(1)−C(1)	132.8(3)	C(14)−Zn(3)−O(2)	133.9(3)	N(7)−Zn(5)−O(1)	93.3(2)
O(1)−Zn(1)−N(2)	91.6(2)	C(14)−Zn(3)−N(3)	117.9(3)	N(6)−Zn(5)−O(2)	93.1(2)
C(1)−Zn(1)−N(2)	118.3(4)	O(2)−Zn(3)−N(3)	91.1(2)	N(7)−Zn(5)−O(2)	122.5(2)
O(1)−Zn(1)−N(1)	103.1(2)	C(14)−Zn(3)−N(4)	107.2(3)	O(1)−Zn(5)−O(2)	92.7(2)
C(1)−Zn(1)−N(1)	108.1(4)	O(2)−Zn(3)−N(4)	103.0(2)	C(28)−Zn(6)−O(1)	133.5(3)
N(2)−Zn(1)−N(1)	96.7(3)	N(3)−Zn(3)−N(4)	97.5(2)	C(28)−Zn(6)−N(7)	117.7(3)
N(2)−Zn(2)−N(3)	126.8(2)	O(2)−Zn(4)−N(6)	91.3(2)	O(1)−Zn(6)−N(7)	91.6(2)
N(2)−Zn(2)−O(1)	92.7(2)	C(15)−Zn(4)−N(5)	108.6(3)	C(28)−Zn(6)−N(8)	107.7(4)
N(3)−Zn(2)−O(1)	124.5(2)	O(2)−Zn(4)−N(5)	103.3(2)	O(1)−Zn(6)−N(8)	103.5(3)
N(2)−Zn(2)−O(2)	125.0(2)	N(6)−Zn(4)−N(5)	97.5(3)	N(7)−Zn(6)−N(8)	96.2(3)
N(3)−Zn(2)−O(2)	92.6(2)	N(6)−Zn(5)−N(7)	128.6(2)	Zn(2)−N(2)−Zn(1)	86.7(2)
O(1)−Zn(2)−O(2)	93.1(2)	N(6)−Zn(5)−O(1)	123.2(2)	Zn(2)−N(3)−Zn(3)	87.3(2)
		Compound **7**			
Zn(1)−C(6)	1.981(9)	Zn(2)−N(2)	2.023(4)	Zn(3)−N(4)	2.093(5)
Zn(1)−O(1)	1.986(5)	Zn(2)−O(1)#1	2.029(4)	Zn(3)−N(3)	2.239(7)
Zn(1)−N(2)	2.091(5)	Zn(2)−Zn(2)#1	2.7657(12)	O(1)−Zn(3)#1	1.973(5)
Zn(1)−N(1)	2.239(7)	Zn(2)−Zn(3)	2.8251(9)	O(1)−Zn(2)#1	2.029(4)
Zn(1)−Zn(2)	2.8241(9)	Zn(3)−O(1)#1	1.973(5)		
Zn(2)−N(4)	2.001(6)	Zn(3)−C(13)	2.004(8)		
C(6)−Zn(1)−O(1)	132.0(3)	N(2)−Zn(2)−Zn(2)#1	116.2(2)	O(1)#1−Zn(3)−N(3)	102.5(3)
C(6)−Zn(1)−N(2)	125.9(4)	O(1)−Zn(2)−Zn(2)#1	47.03(10)	C(13)−Zn(3)−N(3)	111.3(3)
O(1)−Zn(1)−N(2)	90.9(2)	O(1)#1−Zn(2)−Zn(2)#1	46.87(10)	N(4)−Zn(3)−N(3)	83.0(2)
C(6)−Zn(1)−N(1)	111.3(3)	N(4)−Zn(2)−Zn(1)	146.4(2)	O(1)#1−Zn(3)−Zn(2)	45.89(11)
O(1)−Zn(1)−N(1)	101.9(3)	N(2)−Zn(2)−Zn(1)	47.70(14)	C(13)−Zn(3)−Zn(2)	154.4(3)
N(2)−Zn(1)−N(1)	82.9(2)	O(1)−Zn(2)−Zn(1)	44.7(2)	N(4)−Zn(3)−Zn(2)	45.0(2)
C(6)−Zn(1)−Zn(2)	154.5(3)	O(1)#1−Zn(2)−Zn(1)	117.72(14)	N(3)−Zn(3)−Zn(2)	92.3(2)
O(1)−Zn(1)−Zn(2)	45.6(10)	Zn(2)#1−Zn(2)−Zn(1)	79.51(3)	Zn(2)−N(2)−Zn(1)	87.2(2)
N(2)−Zn(1)−Zn(2)	45.1(2)	N(4)−Zn(2)−Zn(3)	47.7(2)	Zn(2)−N(4)−Zn(3)	87.3(2)
N(1)−Zn(1)−Zn(2)	92.3(2)	N(2)−Zn(2)−Zn(3)	146.6(2)	Zn(3)#1−O(1)−Zn(1)	132.9(2)
N(4)−Zn(2)−N(2)	128.0(2)	O(1)−Zn(2)−Zn(3)	117.36(14)	Zn(3)#1−O(1)−Zn(2)	126.5(3)
N(4)−Zn(2)−O(1)	123.7(3)	O(1)#1−Zn(2)−Zn(3)	44.3(2)	Zn(1)−O(1)−Zn(2)	89.5(2)
N(2)−Zn(2)−O(1)	92.4(2)	Zn(2)#1−Zn(2)−Zn(3)	79.30(3)	Zn(3)#1−O(1)−Zn(2)#1	89.8(2)
N(4)−Zn(2)−O(1)#1	92.0(2)	Zn(1)−Zn(2)−Zn(3)	158.81(3)	Zn(1)−O(1)−Zn(2)#1	125.9(3)
N(2)−Zn(2)−O(1)#1	124.6(3)	O(1)#1−Zn(3)−C(13)	131.6(3)	Zn(2)−O(1)−Zn(2)#1	86.09(13)
O(1)−Zn(2)−O(1)#1	93.90(13)	O(1)#1−Zn(3)−N(4)	90.9(2)		
N(4)−Zn(2)−Zn(2)#1	115.8(2)	C(13)−Zn(3)−N(4)	125.9(4)		

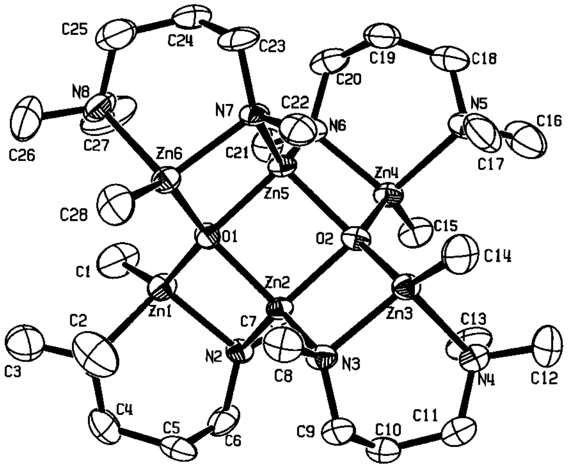

Figure 5. Structure of $Me_4Zn_6O_2[NMe(CH_2)_3NMe]_4$.

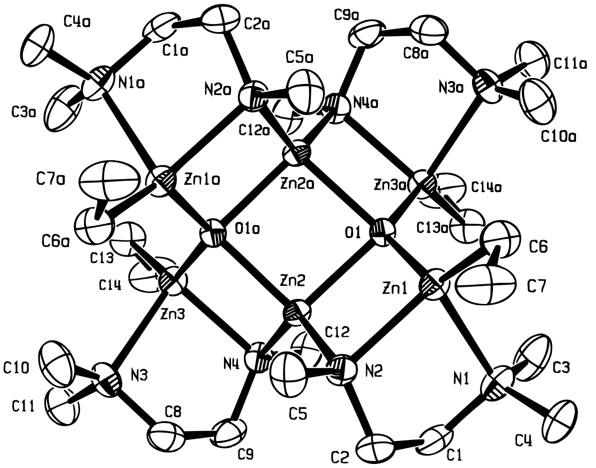

Figure 6. Structure of $Et_4Zn_6O_2[NMe(CH_2)_2NMe]_4$.

$Zn[N(SiMe_3)(OR)]$ (R = 2,6-($^iPr)_2C_6H_3$) (1.95(5), 1.94(5), 1.96(4) Å),[25] [{η^2-$H_2B(3$-$^tBuPz)$}Zn(μ-OH) (1.92(8), 1.98(8), 1.96(1), 1.97(9) Å),[43] and $[EtZn(OC(Me)CHN(Et)(^tBu))]_2$ (2.02(1) Å),[44] slightly longer than those of $[EtZn(NHPh)THF]_3$ (2.29(1), 2.17(1), and 2.26(2) Å),[24] [EtZn(THF)NHMes] (2.24(5), 2.32(5) Å),[24] $[Et_2Zn_4(NHDipp)_4(OEt)_2$ (2.08(4), 2.13(4), 2.18(4) Å),[24] {Zn(μ-$OCEt_3$)$[N(SiMe_3)_2]$}[41] (1.93(3) Å), [Zn(1,4,7-η^3-$OCHCHNMeCH_2NMe_2)_2$][41] (1.99 (3) Å), and $[Zn(OAr)_2(THF)_2]$[44] (1.89(1) Å), but shorter than those observed in the methoxide tetramer[39] (2.09 Å), $[Zn(CCPh)_3(THF)^-$ (2.24(5) Å).[26] Zn−N distances are close to those in $ZnCl_2(TMEDA)$[46] (2.06(1) Å) and $[EtZn(OC(Me)CHN(Et)(^tBu))]_2$ (2.21(1) Å)[33] but considerably shorter in {Zn(μ-$OCEt_3$)$[N(SiMe_3)_2]$}[41] (1.87(3) Å) and longer in [Zn(1,4,7-η^3-$CHCHNMeCH_2NMe_2)_2$][41] (2.27−2.35(4) Å). Zn−C distances in both compounds are unexceptional (1.97−1.99 Å).

The structures of the dimeric compounds (**1**, **2**, **4**, **5**) are based upon the same basic skeleton as those of alky(dialkydithio- or diselenocarbamato)zinc/cadmium(II) complexes reported previously by us.[22,47−50] The basic dimeric skeleton is comprised of three four-membered rings in which one of the chelating sulfur atoms from each ligand is bridging between two zinc atoms to produce a centered four-membered ring and the other two four-membered rings are formed on both sides through a zinc, bridging sulfur, nonbridging sulfur, and carbon atoms. The only difference for these four structures is that each consist of a central four-membered ring formed through a bridging nitrogen instead of sulfur from each ligand and that the side rings are either five- or six-membered rings instead of four-membered. The compounds **6** and **7** have unusual planar structures centered on an oxygen atom, an unusual structural motif.

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Supporting Information Available: Tables of crystal structure and data refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for compounds **1**, **2**, and **4**−**7** (48 pages). Ordering information is given on any current masthead page.

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