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Zinc Hydrazide and Zinc Alkoxide Hydrazide Cages with Zn_4N_8 and Zn_4N_6O Cores – Cluster Isomerism as a Result of Subtle Changes in Ligand Size

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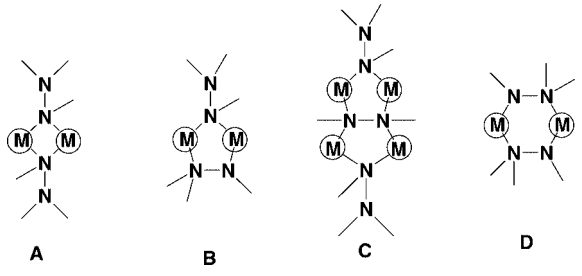
The hydrazide cluster $[(i\text{PrZn})_4(NHNMe_2)_4]$ (**1**) was synthesised by the reaction of diisopropylzinc with *N*,*N*-dimethylhydrazine and was characterised by ^1H- and ^{13}C NMR and IR spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography. This compound forms asymmetric aggregates containing Zn_4N_8 cores. The Zn atoms in these aggregates are arranged in topological tetrahedra in which the triangular faces are bridged by $NHNMe_2$ substituents. Each NH group is connected to two Zn atoms and each NMe_2 group to one Zn atom. Alkoxide clusters were prepared in one-pot syntheses by treating diisopropylzinc solutions with mixtures of *N*,*N*-dimethylhydrazine and ROH (R = Et, *i*Pr). The resulting compounds have the formula $[(i\text{PrZn})_4(NHNMe_2)_3(OR)]$ [R = Et (**3**), *i*Pr(**4**)] and contain Zn_4N_6O cages, such that one $NHNMe_2$ in **1** is replaced by one alkoxide group. Two different aggregation modes were found for these Zn_4N_6O cages. In compound **3**, one Zn atom is bound to two NMe_2 groups and one NH group. The other three Zn atoms each have three bonds to NH groups and one dative bond to an NMe_2 group. The cage consists of one four-membered and one six-membered ring as well as four five-membered rings. In compound **4**, the fourth zinc atom is exclusively bonded to three anionic NH functions in such a way that the rings in the cage are all five-membered. Compounds **3** and **4** were characterised by NMR spectroscopy and single-crystal X-ray diffraction. Hydrazide hydroxide clusters were also obtained through the reaction of a diisopropylzinc solution with *N*,*N*-dimethylhydrazine and a small amount of water. The structure of the resulting cocrystalline material, $[(i\text{PrZn})_4(NHNMe_2)_4]\cdot[(i\text{PrZn})_4(NHNMe_2)_3(OH)]$ (**2**), was also confirmed by X-ray diffraction. The hydroxide cluster in **2** contains a Zn_4N_6O cage, with a similar aggregation mode to that of **4**.

Introduction

The great variety of the chemistry of group 13 metal hydrazides has recently been reviewed by Uhl.[1] Such metal hydrazides can be employed as single-source precursors for the generation of metal nitrides[2] by CVD methods, although they have been applied in this context less frequently than metal amides.[3] The compounds reported include simple dimers like $[(Me_2Al\text{-}\mu\text{-}NHNMe_2)_2]$,[4] trimers like $[(Me_2Ga\text{-}\mu\text{-}NHNMe_2)_3]$[5] or more complex ladder-type aggregates such as $[Al_4(NHNMe_2)_8(NNMe_2)_2]$.[6] The different aggregation modes in such metal hydrazides originate from the presence of two directly connected inequivalent donor sites. Scheme 1 shows some examples of typical bridging modes realised in various metal hydrazides.



Scheme 1.

A few of these hydrazides also show β-donor bonding leading to three-membered AlNN units.[7a–7e] The reaction between hydrazine, N_2H_4, and $GaMe_3$ affords a singular bicyclic compound, $[(Me_2Ga)_4(N_2H_2)(NHNH_2)_2]$,[8] in which two five-membered heterocycles are connected by a common N–N bond and also have N–NH_2 groups in exocyclic positions as in type C. A high degree of coordinative flexibility has also recently been documented for the related hydroxylamides in organoaluminium and -gallium chemistry; examples of the corresponding four-, five- and six-membered ring isomers have been reported.[9]

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On the basis of these results, it seems surprising that a corresponding organometallic chemistry with group 12 elements, in particular with zinc, which neighbours gallium, has not been extensively established so far. Zinc alkoxides are a well-established class of compounds.[10] They include homoleptic compounds,[10b] alkylzinc alkoxide clusters,[10c] and the zinc siloxide clusters, which have been described as early as 1960 by Schmidbaur and co-workers[10d,10e] and have recently been investigated by Driess and co-workers, who uncovered new varieties of aggregation and interesting thermolysis behaviour.[10f–10h] The only known hydrazide of zinc was $[Zn(N_2H_3)_2]$,[11] but this compound is quite cumbersome to synthesise and furthermore has the disadvantage of containing the N_2H_3 group, which exhibits a considerable explosion hazard. In our recent work, we have synthesised the first organometallic zinc hydrazide clusters of the type $[(RZn)_4(NHNMe_2)_4]$ (R = Me, Et) and their alkoxide and hydrazide hydroxide derivatives.[12] Hydrazides of other divalent metal ions have been described, examples include the magnesium hydrazides $\{Mg[NPhN(SiMe_3)_2]_2\}$ and $\{Mg[N(SiMe_3)NMe_2]_2\}$[13] and the beryllium hydrazide $[Be(NMeNMe_2)_2]$.[14] The results of these investigations can be compared with the better established chemistry of the alkali metal hydrazides, in particular that of lithium, which has a large variety of structural motifs.[15–21]

The driving force for preparing these zinc hydrazides and their oxygen derivatives is to explore their aggregation chemistry and behaviour in pyrolysis. Zinc oxide is a widely used semiconductor as it has a wide bandgap. The substitution of oxide by nitride in zinc-based materials such as ZnO would result in a *p*-type semiconductor, which was so far only realised with Ga codoping or by treatment with active nitrogen or with nitrogen oxides such as N_2O.[22a–22c] However, these substitution processes show poor reproducibility. The synthesis of such materials by using a molecular precursor route has not been tried to date, probably because of the restricted number of readily accessible thermolabile Zn/N precursor compounds.

In this contribution, we report the synthesis of new organozinc hydrazides and derivatives thereof in which hydrazide units are replaced by hydroxide or alkoxide units. This will be the starting point for the exploration of a new class of compounds, which could possibly be used as molecular precursors for new materials.

Results and Discussion

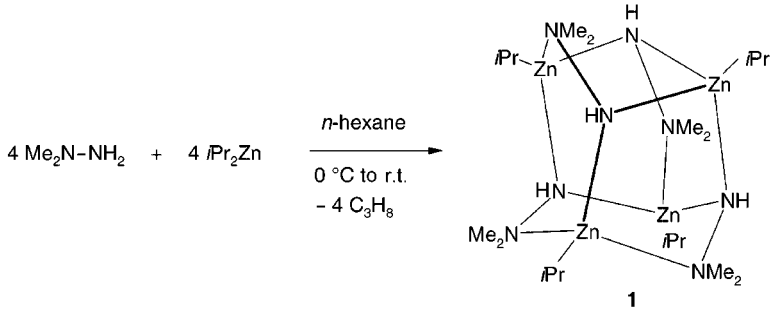
Isopropylzinc Hydrazide

The reaction of diisopropylzinc with *N*,*N*-dimethylhydrazine gives the hydrazide $[(i\text{PrZn})_4(NHNMe_2)_4]$ (**1**) in moderate yield (Scheme 2). It is soluble in all hydrocarbons and ethers and is easily purified by crystallisation. Compound **1** melts at 228–229 °C.

Hydrazide **1** was formed by combining $i\text{Pr}_2\text{Zn}$ and H_2NNMe_2 in a 1:1 ratio and was characterised by NMR spectroscopy and elemental analysis. The presence of tetrameric aggregates was proven by mass spectroscopy; the highest mass found was that of the tetramer minus one isopropyl group. Two bands at 3150 and 3174 cm^{-1} in the IR spectrum proved the presence of NH functions. The ^1H- and ^{13}C NMR spectra in $CDCl_3$ solution indicated the absence of molecular symmetry in the tetramer, as all four hydrazide methyl groups and all four isopropyl groups at zinc gave individual sets of signals. However, it is impossible to prove the formation of a single aggregation type solely from these data. Therefore, analysis by X-ray diffraction was performed on colourless single crystals of **1**, grown by storing an *n*-hexane solution of the compound at –26 °C for several days.

Compound **1** exhibits an unusual M_4N_8 cage structure which is C_1 symmetric (Figure 1). The topology is related to that of $[(MeGa)_4(NHNPh)_4]$, which contains a Ga_4N_8 cage and a dianionic ligand compensating for the formal double charge of the cationic unit $MeGa^{2+}$.[23] There is also a structural resemblance to the zinc oximate $[(MeZn)_4(ONCMe_2)_4]$, which also has a $Zn_4N_4O_4$ core,[24] but has oxygen as the primary binding atom. Furthermore, the structure is similar to the dimethyl- and diethylhydrazides $[(RZn)_4(NHNMe_2)_4]$ (R = Me, Et) recently reported by us.[12]

In compound **1**, all the zinc and nitrogen atoms have coordination number four. There are altogether six rings, two of which are six-membered (Zn_2N_4) and four are five-membered (Zn_2N_3). The zinc atoms in **1** span a topological tetrahedron, each one of whose four triangular faces are capped by a hydrazide ligand. Each hydrazide unit forms two bonds to zinc atoms from its NH group and one dative bond from its NMe_2 group. The distribution of these types of bonds is uneven: Zn1 has three bonds to NH units, Zn2



Scheme 2.

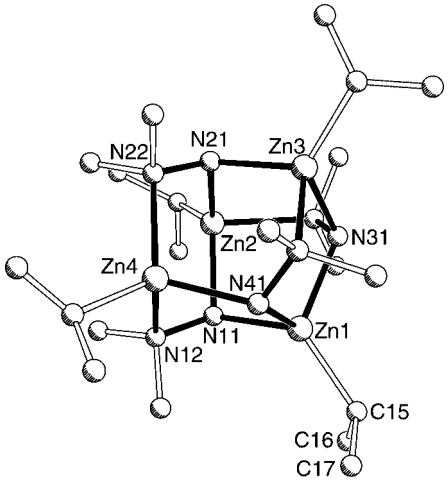


Figure 1. Molecular structure of $[(i\text{PrZn})_4(\text{NHNMe}_2)_4]$ (**1**) as determined by X-ray crystallography. Hydrogen atoms are omitted for clarity.

and Zn3 have two to NH units and one to an NMe_2 group, and finally Zn4 has one bond to an NH unit and two to NMe_2 groups. The bonds from the Zn atoms to the formally anionic NH groups are shorter by more than 0.1 Å than those to the NMe_2 groups. Table 1 lists selected geometric parameters for **1**.

Table 1. Selected bond lengths [Å] and angles [°] for $[(i\text{PrZn})_4(\text{NHNMe}_2)_4]$ (**1**) as determined by X-ray crystallography.

Bond lengths		Angles	
Zn1–C15	2.011(8)	C15–Zn1–N11	122.0(3)
Zn1–N11	2.094(6)	C15–Zn1–N31	120.8(3)
Zn1–N31	2.066(6)	C25–Zn2–N21	124.5(4)
Zn1–N41	2.064(7)	Zn1–N11–Zn2	106.4(3)
Zn2–N11	2.039(7)	Zn1–N11–N12	110.7(3)
Zn2–N21	2.059(8)	Zn2–N32–C33	109.2(6)
Zn2–N32	2.150(6)	N11–Zn1–N31	95.5(2)
N11–N12	1.436(9)	N31–Zn1–N41	97.6(3)

Isopropylzinc Hydrazide Hydroxide

We have previously reported the formation of the mixed hydrazide hydroxide clusters $[(\text{MeZn})_4(\text{NHNMe}_2)_3(\text{OH})]$ and $[(\text{EtZn})_4(\text{NHNMe}_2)_3(\text{OH})]$[12] from the one-pot reaction between dimethyl- or diethylzinc, *N*,*N*-dimethylhydrazine and water. By carrying out the reaction under similar conditions, but with diisopropylzinc as the organometallic component, we expected to obtain $[(i\text{PrZn})_4(\text{NHNMe}_2)_3(\text{OH})]$. Unexpectedly, the cocrystalline compound $[(i\text{PrZn})_4(\text{NHNMe}_2)_4]\cdot[(i\text{PrZn})_4(\text{NHNMe}_2)_3(\text{OH})]$ (**2**) (Scheme 3) formed and was characterised by single-crystal X-ray diffraction. The presence of the OH group was also confirmed by IR spectroscopy. In the ^{1}H NMR spectrum, we could find three sets of signals for the hydrogen atoms at the isopropyl groups. Adding larger amounts of water to the mixture of diisopropylzinc and *N*,*N*-dimethylhydrazine leads to the formation of complicated mixtures of compounds and insoluble precipitates, which could not be separated or identified.

Compound **2** is very soluble in *n*-hexane and in ethereal solvents. Single crystals were obtained by cooling an *n*-hexane solution of **2** for several days at –26 °C.

The crystals of **2** adopt the monoclinic space group $P2_1/c$ and comprise M_4N_8 and M_4N_6O cores (Figure 2). Selected geometric parameters for **2** are listed in Table 2.

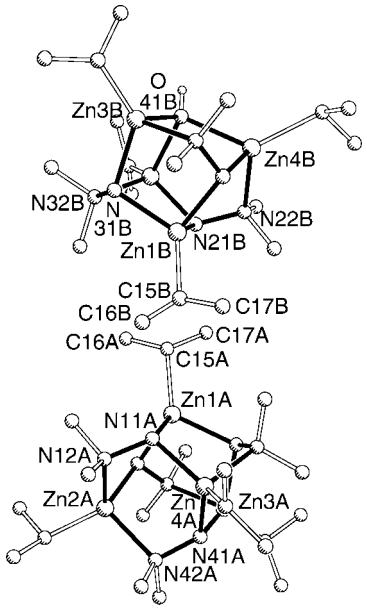
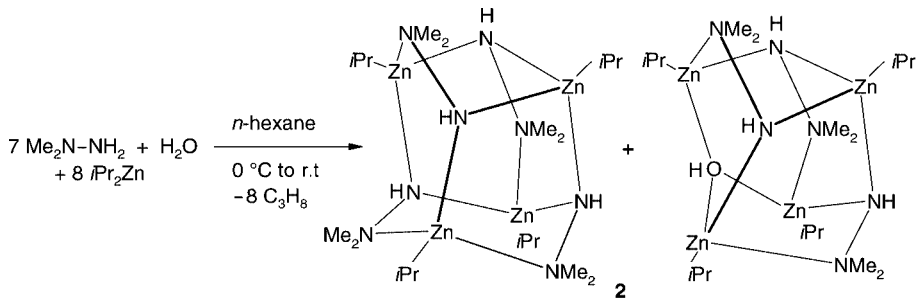


Figure 2. Molecular structure of the cocrystalline compound $[(i\text{PrZn})_4(\text{NHNMe}_2)_4]\cdot[(i\text{PrZn})_4(\text{NHNMe}_2)_3(\text{OH})]$ (**2**) as determined by X-ray crystallography. Hydrogen atoms except the one bound to oxygen are omitted for clarity.



Scheme 3.

Table 2. Selected bond lengths [Å] and angles [°] for $[(i\text{PrZn})_4(\text{NHNMe}_2)_4]\cdot[(i\text{PrZn})_4(\text{NHNMe}_2)_3(\text{OH})]$ (**2**) as determined by X-ray crystallography. Each Zn cage appears as a separate column.

$[(i\text{PrZn})_4(\text{NHNMe}_2)_4]$		$[(i\text{PrZn})_4(\text{NHNMe}_2)_3(\text{OH})]$	
Zn1A-C15A	2.014(7)	Zn1B-C15B	2.000(15)
Zn1A-N21A	2.081(6)	Zn1B-N21B	2.080(9)
Zn1A-N11A	2.073(6)	Zn1B-N31B	2.082(9)
Zn1A-N31A	2.083(5)	Zn2B-C25B	2.012(15)
Zn2A-C25A	2.014(9)	Zn2B-N21B	2.025(8)
Zn2A-N21A	2.048(6)	Zn2B-N12B	2.150(6)
Zn2A-N12A	2.139(8)	N11B-N12B	1.444(11)
N11A-N12A	1.472(9)	O41B-Zn2B	2.226(11)
C15A-Zn1A-N21A	121.0(3)	O41B-Zn3B	2.175(12)
C15A-Zn1A-N11A	122.4(3)	C15B-Zn1B-N11B	118.1(6)
C15A-Zn1A-N31A	118.3(3)	C15B-Zn1B-N31B	122.9(8)
N21A-Zn1A-N11A	94.9(3)	N21B-Zn1B-N11B	96.5(4)
N21A-Zn1A-N31A	98.0(2)	N21B-Zn1B-N31B	95.8(4)
N11A-Zn1A-N31A	96.5(2)	Zn1B-N21B-Zn2B	104.4(4)
Zn1A-N21A-Zn2A	108.9(3)	Zn1B-N21B-N22B	109.2(7)
Zn1A-N21A-N22A	110.1(4)	Zn2B-O41B-Zn3B	98.7(6)

Isopropylzinc Monoalkoxide Trihydrazide

In order to obtain zinc alkoxide hydrazide compounds, we combined dialkylzinc solutions, alcohol and hydrazine in one-pot syntheses. To achieve the formation of monoalkoxide clusters, a diisopropylzinc/hydrazine/alcohol ratio of 4:2.4:2 was employed (Scheme 4). From this mixture we obtained the compounds $[(i\text{PrZn})_4(\text{NHNMe}_2)_3(\text{OR})]$ [R = Et (**3**), *i*Pr(**4**)]. In an earlier publication, we mentioned the formation of similar products by alcoholysis of the pure hydrazides with dimethyl- and diethylzinc units.[12]

The ^{1}H and ^{13}C NMR spectra of **3** and **4** show one set of alcoholate signals and three sets of signals for the hydrogen atoms at isopropyl groups. The integration ratio gives a zinc alkyl/hydrazide/alkoxide stoichiometry of 4:3:1. The IR spectra show bands corresponding to NH stretching modes. The highest peak in the mass spectrum corresponds to the mass of the molecular cations minus the mass of the alkyl group attached to the O atom. Compounds **3** and **4** melt at 195 °C and 223 °C, respectively. They are soluble in hydrocarbons and ethereal solvents.

The structures of **3** and **4** were obtained by single-crystal X-ray diffraction (Figure 3 and Figure 4). The compounds crystallise in the monoclinic space groups $P2_1/n$ and $P2_1/c$, respectively, from *n*-hexane solutions upon cooling to –26 °C for several days.

The quality of the diffraction data for compound **3** was poor, mainly because of the conformational flexibility of the isopropyl groups, as we frequently observe in this area of chemistry. Therefore, the structural data, which we provide here for the purpose of comparison, should not be overinterpreted.

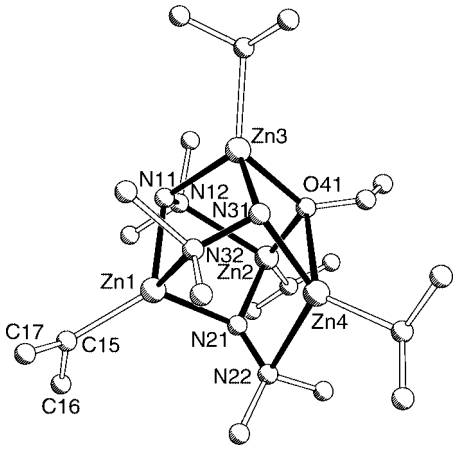
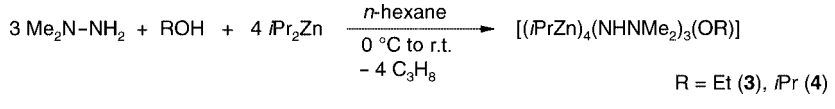


Figure 3. Molecular structure of $[(i\text{PrZn})_4(\text{NHNMe}_2)_3(\text{OEt})]$ (**3**) as determined by X-ray crystallography. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–N21 2.040(12), Zn1–N11 2.057(11), Zn1–N32 2.17(2), Zn2–N21 2.001(12), Zn2–N12 2.199(12), O41–Zn2 2.018(15), O41–Zn3 1.989(18), O41–Zn4 2.34(3); C15–Zn1–N21 122.3(9), C15–Zn1–N11 123.7(10), C15–Zn1–N32 119.1(8), N21–Zn1–N11 94.3(5), N11–Zn1–N32 88.7(8), Zn1–N21–N22 123.1(11), O41–Zn3–N11 91.0(5), Zn2–O41–Zn3 111.9(7).

Both **3** and **4** contain Zn_4N_6O cores in their molecular structures. We found two different types of aggregation mode in the crystal cores of **3** and **4**. In **3**, the three zinc atoms that are connected to oxygen form one bond to an anionic NH unit and one dative bond to an NMe_2 group. The fourth zinc atom is bound to one NH unit and forms two dative bonds to NMe_2 groups. Therefore, compound **3**



Scheme 4.

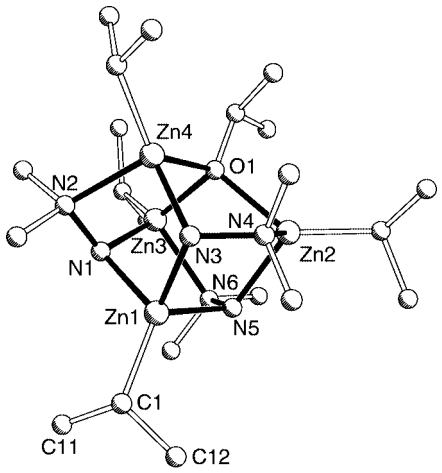


Figure 4. Molecular structure of one of the two independent molecules of $[(i\text{PrZn})_4(\text{NHNMe}_2)_3(\text{O}i\text{Pr})]$ (**4**) as determined by X-ray crystallography. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–C1 2.016(7), Zn1–N1 2.067(6), Zn2–N5 2.041(5), Zn2–N4 2.150(6), O1–Zn2 2.117(5), O1–Zn4 2.142(6); C1–Zn1–N1 121.3(3), N1–Zn1–N5 94.8(2), N1–Zn1–N3 92.9(3), Zn1–N1–Zn3 107.6(3), O1–Zn3–N1 92.2(3), Zn2–O1–Zn3 108.0(2).

forms one four-membered Zn_2NO and one six-membered Zn_2N_4 ring as well as two five-membered Zn_2N_3 and two five-membered Zn_2N_2O rings. By contrast, in compound **4**, the fourth zinc atom, which is not connected to the oxygen atom, bonds to three anionic NH units, allowing all six rings to be five-membered (Figure 5). This shows that subtle changes in the sizes of the oxygen substituents can lead to substantial variations in the cage structure of such aggregates. On the other hand, these results indicate that such different cage constitutions vary only slightly in energy.

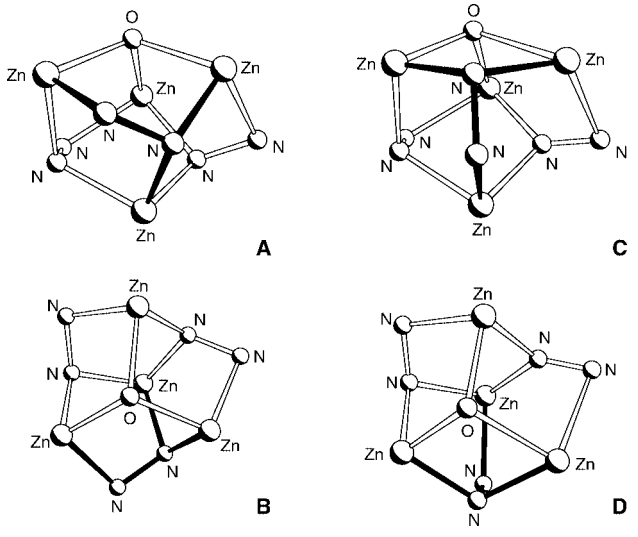


Figure 5. Illustration of the possible aggregation isomers of one of the hydrazide units at the common core structure $Zn_4(\text{NHNMe}_2)_2(\text{OR})$ in $[(i\text{PrZn})_4(\text{NHNMe}_2)_3(\text{OEt})]$ (**3**, **C** and **D**) and $[(i\text{Pr}_2\text{Zn})_4(\text{NHNMe}_2)_3(\text{O}i\text{Pr})]$ (**4**, **A** and **B**). Only the two different Zn_4N_6O cores are shown in two views rotated by about 90°. The structures of the common $Zn(N_2)_2(O)$ cores of the $Zn_4(\text{NHNMe}_2)_2(\text{OR})$ units are shown in hollow lines, the orientation of the N_2 unit of the NHNMe_2 group and its connection to the rest of the structure are shown in filled lines.

Experimental Section

General Considerations: All manipulations of air-sensitive compounds were carried out under a dry nitrogen atmosphere with standard Schlenk and high-vacuum techniques by using double manifolds or in a glovebox operated under argon. Solvents were purified and dried by standard methods immediately prior to use. *N*,*N*-Dimethylhydrazine was purchased from Aldrich Chemical Company and dried by distillation from CaH_2 under dry nitrogen. Diisopropylzinc was synthesised according to a literature procedure.[25] ^{1}H and ^{13}C NMR spectra were recorded with a Varian Inova-300, 400, 500 or a Varian Unity Plus 600 spectrometer in $CDCl_3$ which was dried with activated molecular sieves. ^{1}H- and ^{13}C assignments were confirmed when necessary by use of two-dimensional ^{1}H–^{1}H and ^{13}C–^{1}H correlation NMR experiments. All spectra were recorded at 25 °C and referenced internally to residual protiosolvent (^{1}H) or solvent (^{13}C) resonances. Chemical shifts are quoted in ppm and coupling constants in Hz. A Nonius Kappa-CCD (λ = 0.71073 Å) (for compounds **1**, **2** and **3**) or a Bruker Smart CCD X-ray diffractometer (λ = 1.54184 Å) (for compound **4**) was used to collect the scattering intensities for single-crystal X-ray diffraction experiments. IR spectra were measured with a Bruker IFS (103 V) by using KBr pellets prepared in the glovebox.

$[(i\text{PrZn})_4(\text{NHNMe}_2)_4]$ (1): $i\text{Pr}_2\text{Zn}$ (8.00 mL of a 2.5 M solution in *n*-hexane/diethyl ether; 20.0 mmol) was added dropwise with a syringe to a stirred solution of $H_2\text{NNMe}_2$ (2.30 mL, 30.0 mmol) in *n*-hexane (20 mL) at 0 °C. The reaction mixture was gradually warmed to room temp. and stirred for 6 h. Solvents were removed under reduced pressure The residue was then dissolved in *n*-hexane and filtered. The clear, colourless filtrate was stored at –26 °C to afford colourless, plate-like crystals.

Yield: 63% (2.11 g, 3.14 mmol). M.p. 228–229 °C. ^{1}H NMR (400 MHz): δ = 0.07 [sept, $^3J_{\text{H,H}}$ = 7.7 Hz, 1 H, ZnC*H*], 0.14–0.30 [m, 2 H, ZnC*H*], 0.37 [sept, $^3J_{\text{H,H}}$ = 7.7 Hz, 1 H, ZnC*H*], 1.13–1.25 [m, 24 H, $\text{ZnCH}(\text{C}H_3)_2$], 2.06, 2.09, 2.12 [s, 4 H, N-*H*], 2.23–2.77 [m, 24 H, $\text{N}(\text{C}H_3)_2$] ppm. ^{13}C{^{1}H} NMR (125.7 MHz): δ = 10.22, 11.07, 11.32, 11.69 [Zn*C*H], 24.73, 24.89, 25.15, 25.31, 25.33, 25.50, 25.59, 25.73 [$\text{ZnCH}(C\text{H}_3)_2$], 53.87, 54.76, 55.14, 55.64, 56.51, 56.83, 57.14, 57.89 [$\text{N}(C\text{H}_3)_2$] ppm. $C_{20}H_{56}N_8Zn_4$ (670.24): calcd. C 35.83, H 8.42, N 16.72; found C 35.75, H 8.21, N 16.38. EI-MS [*m*/*z* (%)]: 627 (100), $[\text{M}^+-\text{C}_3\text{H}_7]$, 567 (53), $[\text{M}^+-\text{C}_3\text{H}_7-(\text{NHNMe}_2)]$, 459 (78), $[\text{M}^+-2\ \text{C}_3\text{H}_7-(\text{NHNMe}_2)]$. IR (KBr): $\tilde{\nu}$ = 3150, 3174 (w, N–H), 2867 (vs), 2821 (vs), 2693 (w), 1465(vs) 1161 (s), 994 (s) 951 (s), 820 (vs), 571 (s) cm^{-1}.

$[(i\text{PrZn})_4(\text{NHNMe}_2)_4]\cdot[(i\text{PrZn})_4(\text{NHNMe}_2)_3(\text{OH})]$ (2): $i\text{Pr}_2\text{Zn}$ (4.00 mL, 2.5 M in *n*-hexane/diethyl ether, 10.0 mmol) was added dropwise with a syringe to a stirred solution of $H_2\text{NNMe}_2$ (0.60 mL, 7.83 mmol) in *n*-hexane (10 mL) at 0 °C. Water (0.07 mL, 3.88 mmol) was added dropwise with a syringe. The reaction mixture was gradually warmed to room temp. and stirred for 6 h. After removal of the solvent under reduced pressure, the residue was dissolved in *n*-hexane and filtered. Colourless crystals of **2** were obtained by storing an *n*-hexane solution of **2** at –26 °C.

Yield: 62% (1.00 g, 1.54 mmol). M.p. 263–264 °C (decomp.). ^{1}H NMR (300 MHz): δ = 0.21 [sept, $^3J_{\text{H,H}}$ = 7.6 Hz, 1 H, ZnC*H*-$(\text{CH}_3)_2$], 0.44 [sept, $^3J_{\text{H,H}}$ = 7.6 Hz, 1 H, $\text{ZnC}H(\text{CH}_3)_2$], 0.83 [sept, $^3J_{\text{H,H}}$ = 7.5 Hz, 2 H, $\text{ZnC}H(\text{CH}_3)_2$], 1.09–1.29 [m, 24 H, $\text{ZnCH}(\text{C}H_3)_2$], 2.06–2.78 [m, 21 H, N-*H*, $\text{N}(\text{C}H_3)_2$] ppm. ^{13}C{^{1}H}

NMR (125.7 MHz): δ = 11.14, 11.35, 11.60, 11.96, 13.41 [Zn*C*H], 23.74, 25.07, 25.26, 25.68, 25.78, 25.91, 27.63 [ZnCH(*C*H_3)$_2$], 53.78, 54.15, 55.39, 55.94, 56.78, 57.11, 57.44, 58.16 [N(*C*H_3)$_2$] ppm. EI-MS [*m*/*z* (%)]: 627 (100), [$M^+ - C_3H_7$]. IR (KBr): $\tilde{\nu}$ = 3323 (w, O–H), 3147 (w, N–H), 2928 (s), 2863 (vs), 2815 (s), 1451 (vs) 1159 (s), 987 (s) 951 (s), 813 (vs) cm^{-1}.

[(*i*PrZn)$_4$(NHNMe$_2$)$_3$(OEt)] (3): *i*Pr$_2$Zn (8.00 mL of 2.5 M in *n*-hexane/diethyl ether; 20.0 mmol) was added dropwise with a syringe to a stirred solution of H_2NNMe_2 (0.92 mL, 12.0 mmol) and EtOH (0.58 mL, 9.96 mmol) in *n*-hexane (20 mL) at 0 °C. The reaction mixture was gradually warmed to room temp. and stirred for 4 h. After removal of the solvent under reduced pressure, the residue was dissolved in *n*-hexane and filtered. The clear, colourless filtrate was stored at –26 °C to afford colourless crystals of **3**.

Yield: 49% (1.60 g, 2.44 mmol). M.p. 195–196 °C. ^{1}H NMR (300 MHz): δ = 0.50 [sept, $^3J_{H,H}$ = 7.6 Hz, 1 H, ZnC*H*(CH$_3$)$_2$], 0.64 [sept, $^3J_{H,H}$ = 7.6 Hz, 2 H, ZnC*H*(CH$_3$)$_2$], 0.79 [sept, $^3J_{H,H}$ = 7.5 Hz, 1 H, ZnC*H*(CH$_3$)$_2$], 1.12–1.28 [m, 24 H, ZnCH(C*H*$_3$)$_2$], 1.30 [t, $^3J_{H,H}$ = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$], 2.04, 2.10 [s, 3 H, N-*H*], 2.32–2.70 [m, 18 H, N(C*H*$_3$)$_2$], 3.93 [q, $^3J_{H,H}$ = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$] ppm. ^{13}C{^{1}H} NMR (75 MHz): δ = 10.62, 11.81, 12.04, 12.35 [Zn*C*H], 20.98 [OCH$_2$*C*H$_3$], 23.94, 24.02, 24.25, 24.95, 24.74, 24.87, 24.92, 25.15 [ZnCH(*C*H$_3$)$_2$], 53.76, 54.14, 54.37, 54.62, 55.18, 55.46 [N(*C*H$_3$)$_2$], 63.49 [O*C*H$_2$CH$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 3174 (w, N–H), 2865 (vs), 2816 (s), 2700 (w), 1159 (s), 874 (vs) cm^{-1}. $C_{20}H_{54}N_6OZn_4$ (654.19): calcd. C 36.72, H 8.01, N 12.85; found C 36.36, H 8.21, N 12.64.

[(*i*PrZn)$_4$(NHNMe$_2$)$_3$(O*i*Pr)] (4): *i*Pr$_2$Zn (6.00 mL of 2.5 M in *n*-hexane/diethyl ether; 15.0 mmol) was added dropwise with a syringe to a stirred solution of H_2NNMe_2 (0.77 mL, 10.06 mmol) and *i*PrOH (0.45 mL, 7.02 mmol) in *n*-hexane (10 mL) at 0 °C. The reaction mixture was gradually warmed to room temp. and stirred for 4 h. The solvents were removed under reduced pressure, the residue was dissolved in *n*-hexane and filtered. The clear, colourless filtrate was stored at –26 °C to afford colourless crystals of **4**.

Yield: 52% (1.30 g, 1.94 mmol). M.p. 223–224 °C. ^{1}H NMR (500 MHz): δ = 0.31 [sept, $^3J_{H,H}$ = 7.5 Hz, 1 H, ZnC*H*(CH$_3$)$_2$], 0.43 [sept, $^3J_{H,H}$ = 7.5 Hz, 2 H, ZnC*H*(CH$_3$)$_2$], 0.52 [sept, $^3J_{H,H}$ = 7.5 Hz, 1 H, ZnC*H*(CH$_3$)$_2$], 1.15–1.19 [m, 6 H, OCH(C*H*$_3$)$_2$], 1.20–1.32 [m, 24 H, ZnCH(C*H*$_3$)$_2$], 1.91, 1.94, 2.01 [s, 3 H, N-*H*], 2.27–2.70 [m, 18 H, N(C*H*$_3$)$_2$], 4.17 [sep, 1 H, OC*H*(CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (125.7 MHz): δ = 11.10, 13.38, 13.68 [Zn*C*H-(CH$_3$)$_2$], 24.35, 24.37, 24.69, 24.72, 24.91, 24.93 [ZnCH(*C*H$_3$)$_2$], 25.43, 25.50 [OCH(*C*H$_3$)$_2$], 54.17, 54.36, 54.46, 54.83, 54.86, 54.95 [N(*C*H$_3$)$_2$], 68.53 [O*C*H(CH$_3$)$_2$] ppm. EI-MS [*m*/*z* (%)]: 627 (100), [$M^+ - C_3H_7$], 459 (99), [$M^+ - C_3H_7 - C_3H_7ZnOC_3H_7$]. IR (KBr): $\tilde{\nu}$ = 3168 (w, N–H), 2867 (vs), 2829 (vs), 1459 (vs), 1377 (s), 1163 (s), 1114 (s), 996 (s), 939 (s), 817 (vs), 787 (s), 570 (s) cm^{-1}. $C_{21}H_{56}N_6OZn_4$ (670.24): calcd. C 37.63, H 8.42, N 12.54; found C 37.41, H 8.44, N 12.39.

Crystal Structures: Crystals of compounds **1**, **2** and **3** were selected and prepared under perfluoropolyether and mounted in a drop of this solution onto the glass fibre tip of the goniometer head. The crystallographic data sets for compounds **1**, **2** and **3** were collected with a Nonius Kappa CCD diffractometer; the data set for **4** was collected with a Bruker Smart CCD diffractometer. The structures were solved by direct methods and refined with the full-matrix least-squares procedure (SHELXTL[26]) against F^2. Details of the crystal data and refinements are provided in Table 3. The generation of good quality crystals of this class of substance has proven very difficult previously,[12] probably because of the ball-shaped structure of the tetrameric or pseudotetrameric aggregates. Despite the limited accuracy of the geometry parameters which could be achieved with the crystalline materials, the crystal structure determination results give valuable information regarding the constitution of the cluster-like aggregates.

One of the two independent molecules in the crystal of **4** is less well defined than the other. In this molecule, two isopropyl groups were refined as a split model to give abundances for the major disorder components of 0.54 and 0.87. Furthermore, two N–N bonds [N(1)–N(2) and N(9)–N(10)] in this molecule were restrained

Table 3. Crystal and refinement data for the compounds **1**, **2**, **3** and **4**.

	1	**2**	**3**	**4**
Formula	$C_{20}H_{56}N_8Zn4$	$(C_{20}H_{56}N_8Zn_4)\cdot(C_{18}H_{50}N_6OZn_4)$	$C_{20}H_{54}N_6OZn_4$	$C_{21}H_{56}N_6OZn_4$
M_r	670.21	1298.32	656.17	670.20
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
a [Å]	15.978(1)	18.191(1)	13.898(1)	17.651(1)
b [Å]	12.006(1)	19.247(1)	13.515(1)	19.763(1)
c [Å]	16.607(1)	19.101(1)	16.714(1)	18.286(1)
α [°]	90	90	90	90
β [°]	101.30(1)	110.58(1)	100.60(1)	105.29(1)
γ [°]	90	90	90	90
V [Å^3]	3124.0(4)	6260.9(6)	3085.8(4)	6152.9(3)
T [°C]	–75	–75	–75	–153
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
Z	4	4	4	8
$\rho_{calcd.}$ [g·cm^{-3}]	1.425	1.377	1.412	1.447
Crystal size [mm]	0.50×0.50×0.35	0.40×0.25×0.10	0.60×0.25×0.15	0.40×0.18×0.06
λ [Å]	0.71073	0.71073	0.71073	1.54184
μ [mm^{-1}]	3.055	3.047	3.092	3.696
$Refl_{collected}$	18372	36365	14219	33862
$Refl_{unique}$	7442	11015	3991	11349
R_{int}	0.043	0.062	0.051	0.063
R_1/wR_2 [$I > 2\sigma(I)$]	0.079/0.219	0.069/0.185	0.098/0.279	0.082/0.204
R_1/wR_2 (all data)	0.130/0.255	0.137/0.222	0.131/0.319	0.125/0.230
$\Delta\rho_{fin}$ [e·Å^{-3}]	2.18/–1.37	1.28/–1.15	0.85/–0.55	4.06/–1.12
CCDC number	292691	292692	292693	292694

to a length of 1.46 (1) Å and the bonds Zn(4)–N(2) and Zn(7)–N(10) to a length of 2.13(1) Å as they tended to refine to inappropriate values. All the distances (bonding and non-bonding) in the disordered isopropyl groups containing C(7) and C(8) were restrained to the average geometry values for the isopropyl groups in the other, better defined molecule. Crystallographic data (excluding structure factors) for the structures reported in this paper have been forwarded to the Cambridge Crystallographic Data Centre as supplementary publications. The deposition numbers are listed in the last line of Table 3. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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