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Zinc Hydrazides and Alkoxyhydrazides: Organometallic Compounds with Novel Zn_4N_8, Zn_4N_6O and $Zn_4N_4O_2$ Cage Structures

Surajit Jana,[a] Roland Fröhlich,[b] and Norbert W. Mitzel*[a]

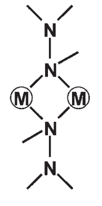
Dedicated to Professor Herbert Schumann on the occasion of his 70th birthday

Abstract: Tetrameric [{RZn(NHNMe$_2$)}$_4$] (R = Me, Et), the first organometallic zinc hydrazides to be described, have been prepared by alkane elimination from dialkylzinc solutions and *N*,*N*-dimethylhydrazine. They were characterised by ^{1}H and ^{13}C NMR and IR spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography. The compounds form asymmetric aggregates containing the novel Zn_4N_8 core; tetrahedra of Zn atoms bear the alkyl groups at Zn, with the triangular faces bridged by NHNMe$_2$ substituents. The NH groups are connected to two Zn atoms, and the NMe$_2$ groups to one. Hydrolysis of the compounds with water gives [(RZn)$_4$(OH)(NHNMe$_2$)$_3$] as products, which also were characterised as described above. Higher yields of these hydroxo clusters were achieved in one-pot syntheses by reaction of dialkylzinc solutions with mixtures of *N*,*N*-dimethylhydrazine and water. They contain Zn_4N_6O cages, in which one hydroxide in the tetrameric hydrazides described above replaces one NHNMe$_2$ group. Similar products can be prepared with alkoxy instead of hydroxy groups, in analogous one-pot syntheses with alcohols. Alcoholysis of [EtZn(NHNMe$_2$)]$_4$ with methanol or ethanol gave zinc trishydrazide monoalkoxides, [(EtZn)$_4$(OR)(NHNMe$_2$)$_3$] (R = Me, Et), which have constitutions analogous to the monohydroxides. The organozinc bishydrazide bisalkoxides [(MeZn)$_4$(NHNMe$_2$)$_2$(OEt)$_2$] and [(EtZn)$_4$(NHNMe$_2$)$_2$(OEt)$_2$] were obtained in one-pot reactions from dialkylzinc solutions with mixtures of the hydrazine and alcohol, and their crystal structures, confirmed by spectroscopic methods in solution, show an unsymmetrical aggregation with the novel $Zn_4N_4O_2$ cage structure.

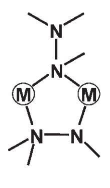
Keywords: cage compounds · hydrazines · N ligands · structure elucidation · zinc

Introduction

Nitrogen-rich hydrazide compounds of the earth metals have been investigated intensively in recent years;[1] the compounds reported include simple dimers such as [{Me$_2$Al-μ-N(H)NMe$_2$}$_2$],[2] trimers such as [{Me$_2$Ga-μ-N(H)-NMe$_2$}$_3$],[3] or the more complex ladder-type aggregate [Al$_4$-(NHNMe$_2$)$_8$(NNMe$_2$)$_2$].[4] The wealth of different aggregation modes in such metal hydrazides originates from the presence of two directly connected donor sites. **A**, **B** and **C** are examples of typical bridging modes that have been found in various metal hydrazides.



A



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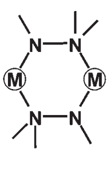

C

A few of these metal hydrazides also show β-donor bonding leading to three-membered AlNN units.[5]

Similar high coordinative flexibility has recently been documented for the related hydroxylamides in organoalu-

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minium and -gallium chemistry, with the corresponding four-, five- and six-membered isomers.[6]

One aim of the numerous studies of Group 13 chemistry with hydrazide substituents was to find new molecular precursors to metal nitride materials (for example, III/V semiconductors). Some hydrazine derivatives of organoaluminium and -gallium compounds have been processed successfully to give AlN and GaN by CVD methods.[7]

In the light of these results it is surprising that a corresponding organometallic chemistry with Group 12 elements, in particular zinc (as the element neighbouring gallium), has not yet been established. The only known hydrazide of zinc is $Zn(N_2H_3)_2$,[8] but this is difficult to prepare and has the disadvantage of containing the N_2H_3 group, which frequently forms compounds of limited stability with a potential explosion hazard. Hydrazides of other two-valent metal ions have been described; examples include the magnesium hydrazides $Mg[NPhN(SiMe_3)_2]_2$ and $Mg[N(SiMe_3)NMe_2]_2$,[9] and the beryllium hydrazide $Be(NMeNMe_2)_2$.[10] The results of these investigations can also be compared with the better established chemistry of the alkali metal hydrazides, in particular that of lithium, which has many varieties of structural motifs.[11–17]

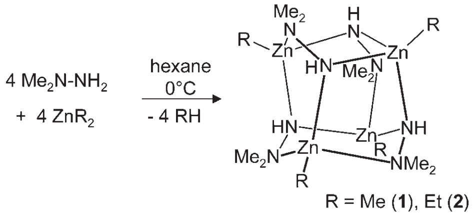
A driving force for establishing routes to zinc hydrazides and derivatives and exploring their aggregation and reactivity is the need to find a molecular precursor route to zinc/nitrogen materials, which has not yet been attempted. The introduction of nitrogen into zinc-based materials such as the wide-bandgap semiconductor ZnO is an interesting preparative target, as it would open up the possibility of producing p-semiconducting zinc oxide by anion substitution with nitride, which so far has only been realised with additional Ga codoping.[18] The chemical synthesis of such materials by a molecular precursor route is difficult because of the restricted number of readily accessible thermolabile Zn/N precursor compounds.

Herein we report the syntheses of the first organometallic zinc hydrazides and derivatives thereof with hydrazide units replaced by hydroxide or alkoxide units. This will be the starting point for exploration of the accessibility and aggregation behaviour of a new class of compounds which can be turned into molecular precursors for new materials.

Results and Discussion

Zinc hydrazides: The reaction of dimethyl- and diethylzinc with *N*,*N*-dimethylhydrazine provides access to organozinc hydrazides in reasonable yields (Scheme 1). These compounds are soluble in hydrocarbons and ethers and can be purified by crystallisation. Compound **2** melts at 202 °C with decomposition, while **1** decomposes before reaching its melting point, which lies above 300 °C.

The 1:1 stoichiometries of zinc atoms to hydrazide units follow from the integration ratio in the ^1H NMR spectra and the elemental analyses. The mass spectra give strong evidence for the presence of tetrameric aggregates, as the highest masses found were those of ions corresponding to the molecular mass of the tetramers minus one alkyl group at the zinc atoms. The IR spectra proved the presence of the NH functions. The ^1H and ^{13}C NMR spectra in solution indicated the absence of molecular symmetry in the tetramers, as all four hydrazide methyl groups and all four alkyl groups at zinc give individual sets of signals. However, with these data it is difficult to prove unequivocally the presence of a single species.



Scheme 1.

Maintaining *n*-hexane solutions of **1** and **2** at −10 °C resulted in precipitation of colourless single crystals, among which so far only those of **2** have been suitable for X-ray diffraction experiments for structure elucidation. Table 1 lists selected geometric parameters for **2**.

Table 1. Selected bond lengths and angles for $[\{EtZn(NHNMe_2)\}_4]$ (**2**) as determined by X-ray crystallography.

Bond lengths [Å]		Angles [°]	
Zn(1)–C(15)	2.016(5)	C(15)-Zn(1)-N(11)	117.3(2)
C(15)–C(16)	1.442(7)	C(15)-Zn(1)-N(21)	119.5(2)
Zn(2)–C(25)	2.010(6)	C(15)-Zn(1)-N(41)	123.4(2)
C(25)–C(26)	1.501(8)	C(25)-Zn(2)-N(21)	125.9(2)
Zn(1)–N(11)	2.079(4)	Zn(1)-N(11)-Zn(3)	104.6(2)
Zn(1)–N(21)	2.092(4)	Zn(1)-N(11)-N(12)	110.7(3)
Zn(1)–N(41)	2.079(4)	Zn(2)-N(12)-N(11)	107.0(3)
Zn(2)–N(21)	2.048(3)	Zn(2)-N(12)-C(13)	117.4(3)
Zn(2)–N(32)	2.155(4)	N(11)-Zn(1)-N(21)	95.6(2)
Zn(2)–N(12)	2.176(4)	N(21)-Zn(1)-N(41)	97.6(2)
N(11)–N(12)	1.450(5)	N(11)-Zn(1)-N(41)	97.7(2)

The structure of **2** has C_1 symmetry (Figure 1); it is a rare case of an M_4N_8 cage structure, and the first to be described for Zn. The topology is in principle related to that of $[\{(MeGa)(NHNPh)\}_4]$, which contains a Ga_4N_8 cage and a dianionic ligand compensating the charge of a formally doubly charged cationic unit $MeGa^{2+}$.[19] There is also a structural relationship to the zinc oximate $[\{(MeZn)(ONCMe_2)\}_4]$ with its $Zn_4N_4O_4$ core,[20] but this has oxygen as the primary bonding atoms.

All zinc and nitrogen atoms in **2** have the coordination number four. The cages of **2** are composed of two six-membered Zn_2N_4 rings and four Zn_2N_3 rings. The zinc atoms in **2** span a topological tetrahedron, which has four triangular faces each capped by a hydrazide ligand. These hydrazide units form two bonds to zinc atoms from the NH groups and a dative one from the NMe_2 groups. The distribution of these types of bonds is uneven: Zn(1) has three bonds to

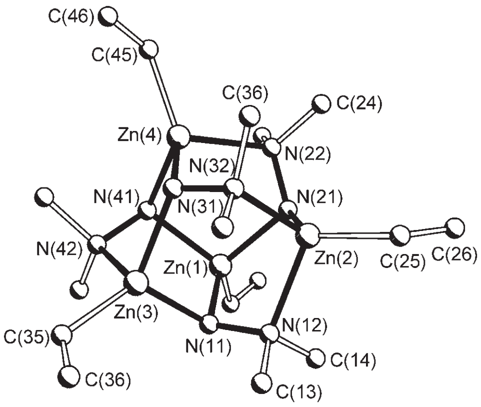
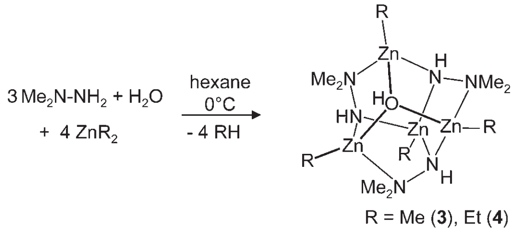


Figure 1. Molecular structure of $[EtZn(NHNMe_2)]_4$ (**2**) as determined by X-ray crystallography. Hydrogen atoms are omitted for clarity.

NH units, Zn(2) and Zn(3) have two to NH units and one to an NMe_2 group, while Zn(4) forms one bond to an NH unit and two to NMe_2 groups. Consequently the clusters are constructed of five- and six-membered rings. The Zn–N bonds between the Zn atoms and the formally anionic NH groups are shorter by more than 0.1 Å than those to the NMe_2 groups, which can be regarded as predominantly dative.

Zinc hydrazide hydroxides: During some of the attempts to prepare **1** and **2** traces of water were present in the systems and gave rise to cluster aggregates, which still contain four alkylmetal units, but three hydrazide units and one hydroxy function. The same compounds could also be obtained if **1** and **2** were dissolved in THF and subsequently hydrolyzed carefully. These procedures, however, led to low yields of a range of different products, which were difficult to separate.

A more convenient route to the mixed hydroxyl/hydrazide aggregates was found in one-pot reactions of dialkylzinc solutions with a mixture of the hydrazine and water (Scheme 2). During optimisation of the reaction conditions, we found that the hydrazine has to be applied in excess, because the reactivity of water toward alkanolysis is higher and can be compensated for in this way. Thus we obtained $[(RZn)_4(OH)(NHNMe_2)_3]$ (R = Me (**3**), Et (**4**)).



Scheme 2.

Compounds **3** and **4** are soluble in hydrocarbon solvents, and more so in ethereal ones. They decompose above 200 °C without reaching a melting point below 300 °C.

The constitutions of **3** and **4** were identified by elemental analyses, ^1H and ^{13}C NMR spectra and mass spectra, and that of **3** additionally by single-crystal X-ray diffraction. The IR spectra show the presence of both OH and NH stretching frequencies. A stoichiometric alkylzinc/hydrazide/hydroxide ratio of 4:3:1 is deduced from the integrals of the proton NMR spectra. The highest peaks in the mass spectra correspond to the masses of $[(RZn)_4(OH)(NHNMe_2)_3]$ cations (R = Me (**3**), Et (**4**)) minus one of the respective alkyl groups at the Zn atoms. The appearance of one set of signals for the $NHNMe_2$ units in both the ^1H and ^{13}C NMR spectra indicates that these compounds adopt higher symmetry than the hydrazides **1** and **2**, which is necessarily threefold according to the composition.

A final structural proof was obtained by single-crystal X-ray diffraction determination of both molecules, **3** and **4** (Figures 2 and 3).

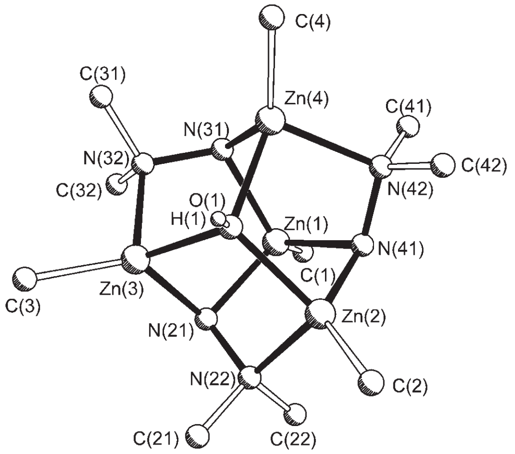


Figure 2. Molecular structure of $[(MeZn)_4(NHNMe_2)_3(OH)]$ (**3**), showing the Zn_4N_6O cage structure. Hydrogen atoms (except in the OH group) are omitted for clarity.

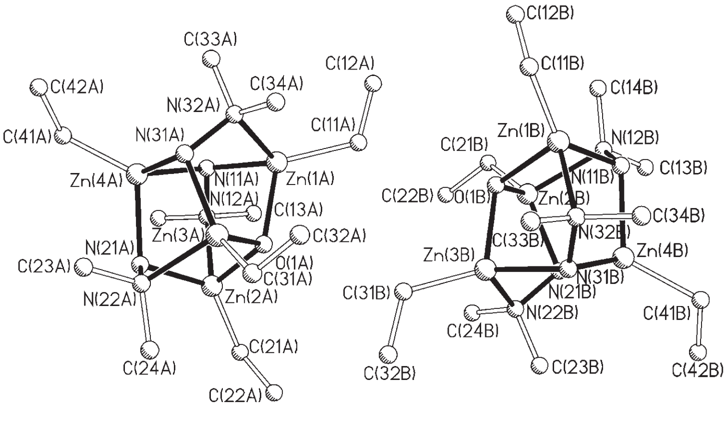


Figure 3. Molecular structure of the two crystallographically independent molecules of $[(EtZn)_4(NHNMe_2)_3(OH)]$ (**4**). Hydrogen atoms are omitted for clarity.

Comparison of selected geometric parameters for **3** and one of the two independent molecules of **4** (Table 2) indicates a close similarity of the structures.

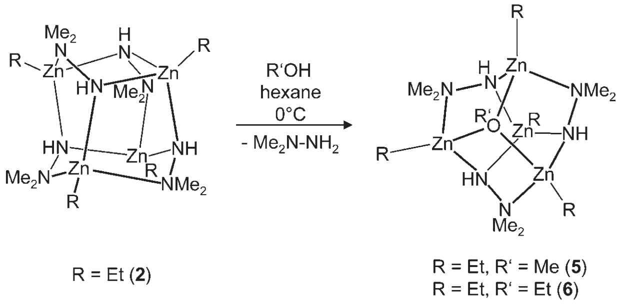
Table 2. Selected bond lengths [Å] and angles [°] for [$(MeZn)_4(NHNMe_2)_3(OH)$] (**3**) and one of the two independent molecules of [$(EtZn)_4(NHNMe_2)_3(OH)$] (**4**) as determined by X-ray crystallography.

[$(MeZn)_4(NHNMe_2)_3(OH)$] (**3**)		[$(EtZn)_4(NHNMe_2)_3(OH)$] (**4**)	
Zn(1)−C(1)	1.995(3)	Zn(4A)−C(41A)	1.989(8)
Zn(1)−N(21)	2.087(2)	Zn(4A)−N(11A)	2.118(6)
Zn(1)−N(31)	2.083(2)	Zn(4A)−N(21A)	2.101(6)
Zn(1)−N(41)	2.105(2)	Zn(4A)−N(31A)	2.089(6)
Zn(2)−C(2)	1.962(3)	Zn(1A)−C(11A)	1.991(10)
Zn(2)−N(22)	2.137(2)	Zn(1A)−N(11A)	2.011(7)
Zn(2)−N(41)	2.026(2)	Zn(1A)−N(32A)	2.149(7)
O(1)−Zn(2)	2.101(2)	O(1A)−Zn(1A)	2.085(5)
O(1)−Zn(3)	2.074(2)	O(1A)−Zn(2A)	2.091(5)
O(1)−Zn(4)	2.090(2)	O(1A)−Zn(3A)	2.084(5)
Zn(3)−N(21)	2.028(2)	Zn(2A)−N(21A)	2.007(6)
N(21)−N(22)	1.458(3)	N(21A)−N(22A)	1.478(8)
N(22)−Zn(2)	2.137(2)	N(22A)−Zn(3A)	2.123(7)
C(1)-Zn(1)-N(21)	120.9(1)	C(41A)-Zn(4A)-N(11A)	119.6(3)
C(1)-Zn(1)-N(31)	122.5(1)	C(41A)-Zn(4A)-N(21A)	120.4(3)
C(1)-Zn(1)-N(41)	118.2(1)	C(41A)-Zn(4A)-N(31A)	122.1(1)
N(21)-Zn(1)-N(31)	96.3(1)	N(11A)-Zn(4A)-N(21A)	96.1(2)
N(21)-Zn(1)-N(41)	96.5(1)	N(11A)-Zn(4A)-N(31A)	96.1(2)
N(31)-Zn(1)-N(41)	96.7(1)	N(21A)-Zn(4A)-N(31A)	96.5(1)
Zn(1)-N(21)-Zn(3)	104.8(1)	Zn(4A)-N(11A)-Zn(1A)	104.6(3)
Zn(1)-N(21)-N(22)	109.9(2)	Zn(4A)-N(11A)-N(12A)	108.9(4)
O(1)-Zn(3)-N(21)	90.8(1)	O(1A)-Zn(1A)-N(11A)	91.5(2)
Zn(2)-O(1)-Zn(3)	107.4(1)	Zn(1A)-O(1A)-Zn(2A)	107.1(2)

All nitrogen, oxygen and zinc atoms in **3** and **4** have the coordination number four. As in **2**, the Zn atoms in **3** and **4** adopt a topological tetrahedral arrangement, with one of the four triangular faces capped by μ_3-bonded OH groups and the other three faces bridged by $NHNMe_2$ units. The zinc atoms bonded to oxygen each form one bond to the anionic NH groups and one dative bond to an NMe_2 group. Predictably, the bonds to the anionic NH functions are shorter than the dative ones to the NMe_2 groups.

The fourth zinc atom is bonded exclusively to the anionic NH functions and to its own alkyl group. In contrast to the completely unsymmetrical tetrameric hydrazides, the structures of the hydroxy aggregates **3** and **4** are thus close to C_3 symmetry, with this axis passing through the O and Zn(1) atoms as well as the hydroxyl proton and the C(1) atom. This explains why the signals in the NMR spectra are consistent with C_3 symmetry and shows that these structures are retained in solution. In **3** and **4** the six rings of the cluster are all five-membered.

Zinc tris(hydrazide) mono(alkoxide)s: As the combination of hydrazide and hydroxide groups into mixed tetranuclear zinc clusters can be achieved in straightforward one-pot syntheses, we wondered whether these results could be transferred to the chemistry of the related alkoxides. The results of these reactions are highly dependent on the stoichiometric ratios of the reactants employed. The best way to synthesise the monoalkoxy clusters turned out to be by alcoholysis of the pure hydrazides (Scheme 3).



Scheme 3.

Owing to decomposition above 200 °C, compounds **5** and **6** cannot be obtained in a molten state at temperatures of up to 300 °C. Both are soluble in hydrocarbon and ethereal solvents.

The ^1H and ^{13}C NMR spectra of **5** and **6** show only one set of resonances belonging to the hydrazide units. The integration ratio gives a zinc alkyl/hydrazide/alkoxy stoichiometry of 4:3:1. The highest peaks in the mass spectra correspond to the masses of the molecular cations minus one ethyl group, pointing to the fragmentation of one Zn−C bond. The presence of NH groups and the absence of OH groups follow from the absorptions found in the IR spectra. Predictably, these data are consistent with the structures of the alkoxides **5** and **6** being analogous to those of the hydroxides **3** and **4**; that is, these alkoxides also have an averaged molecular C_3 symmetry on the NMR spectroscopy timescale.

The crystal structure of **5** (Figure 4; selected bond lengths and angles are listed in Table 3) confirmed the constitution deduced from the spectroscopic data. It crystallises in the monoclinic space group $P2_1/n$ with two molecules per asymmetric unit; that is, there are two crystallographically independent molecules, as in **4**.

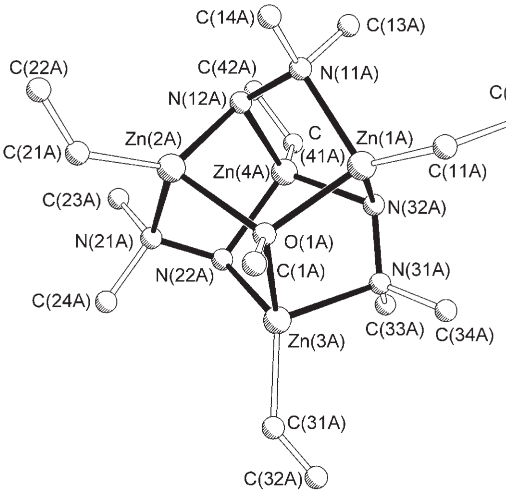
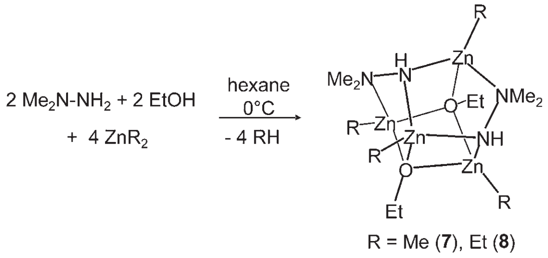


Figure 4. Molecular structure of one of the two crystallographically independent molecules of [$(EtZn)_4(NHNMe_2)_3(OMe)$] (**5**). Hydrogen atoms are omitted for clarity.

Table 3. Selected bond lengths and angles for one of the two independent molecules of $[(EtZn)_4(NHNMe_2)_3(OMe)]$ (**5**) as determined by X-ray crystallography.

Bond lengths [Å]		Angles [°]	
Zn(4A)–C(41A)	1.983(5)	C(41A)-Zn(4A)-N(12A)	121.3(2)
Zn(4A)–N(12A)	2.092(5)	C(41A)-Zn(4A)-N(22A)	120.2(2)
Zn(4A)–N(22A)	2.079(4)	C(41A)-Zn(4A)-N(32A)	120.5(2)
Zn(4A)–N(32A)	2.070(4)	N(12A)-Zn(4A)-N(22A)	96.2(2)
Zn(1A)–C(11A)	1.982(5)	N(12A)-Zn(4A)-N(32A)	96.9(2)
Zn(1A)–N(11A)	2.125(4)	N(22A)-Zn(4A)-N(32A)	95.9(2)
Zn(1A)–N(32A)	2.021(4)	Zn(4A)-N(32A)-Zn(1A)	104.5(2)
O(1A)–Zn(1A)	2.074(4)	Zn(4A)-N(32A)-N(31A)	110.9(3)
O(1A)–Zn(2A)	2.112(4)	O(1A)-Zn(1A)-N(32A)	92.7(2)
O(1A)–Zn(3A)	2.119(4)	Zn(1A)-O(1A)-Zn(2A)	106.6(2)
Zn(2A)–N(21A)	2.121(4)		
N(21A)–N(22A)	1.447(6)		
N(22A)–Zn(3A)	2.005(5)		

Zinc bis(hydrazide) bis(alkoxide)s: The quest for other stoichiometries and aggregation modes of zinc hydrazides/alkoxides led us to attempt successfully the synthesis of hydrazide:alkoxide units in a 1:1 ratio in one-pot reactions of dimethylzinc and diethylzinc with an excess of the hydrazine and ethanol (Scheme 4).



Scheme 4.

The identity of the products was proven by NMR spectroscopy of the ^{1}H and ^{13}C nuclei. There are two different sets of signals for alkoxide units and two sets for the hydrazide units. The IR spectra show bands for NH-stretching modes but no OH bands. In the mass spectra the highest peaks correspond to the masses of the molecular cations minus one ethyl group, pointing to the fragmentation of one O–C bond. Compounds **7** and **8,** also, cannot be obtained in a molten state at temperatures of up to 300 °C. Together with the mass spectra and NMR results, this indicates the presence of C_1-symmetric tetrazinc clusters.

Crystals of **7** and **8** suitable for crystallographic investigations were grown from hexane solution. In both crystal structures (Figures 5 and 6, with selected geometrical parameters in Table 4) there are two crystallographically independent molecules in the asymmetric units of the monoclinic crystals, which are in the space group $P2_1/c$.

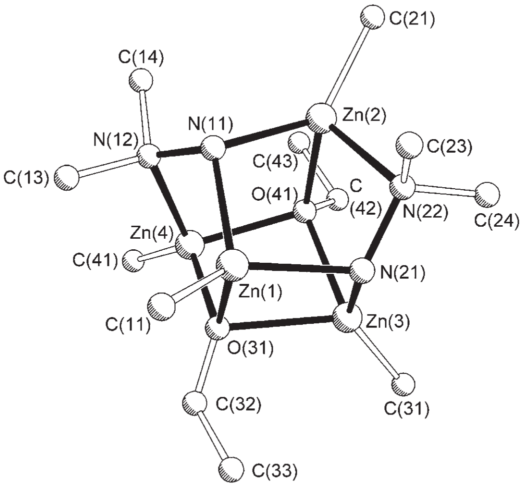


Figure 5. Molecular structure of one of the two crystallographically independent molecules of $[(MeZn)_4(NHNMe_2)_2(OEt)_2]$ (**7**). Hydrogen atoms are omitted for clarity.

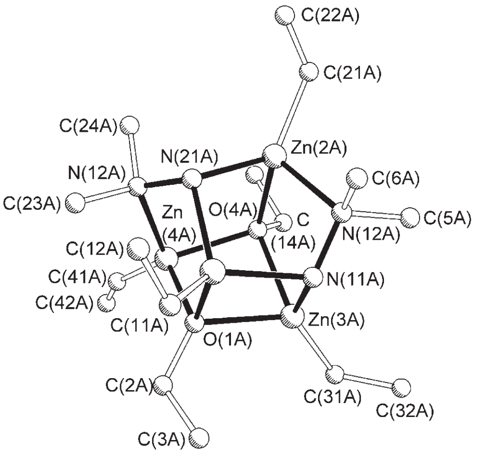


Figure 6. Molecular structure of one of the two crystallographically independent molecules of $[(EtZn)_4(NHNMe_2)_2(OEt)_2]$ (**8**). Hydrogen atoms are omitted for clarity.

The crystal structures confirm that the environments of all the Zn atoms differ from each other. Two of the adjacent rings are four-membered and the other four rings are five-membered. In **7** Zn(1) is bonded to a methyl group, two anionic NH functions and an oxygen atom, and it is involved in one four- and two five-membered rings. Zn(2) is bonded to a methyl group, one anionic NH group, a neutral NMe_2 group and one oxygen atom, and it is involved in three five-membered rings. Zn(3) is bonded to a methyl group, two oxygen atoms and one anionic NH group, and it is involved in one five- and two four-membered rings. Zn(4) is bonded to a methyl group, two oxygen atoms and one neutral NMe_2 group, and it is involved in one four- and two five-membered rings. The situation in **8** is analogous.

Conclusion

We have firmly established, through structural and spectroscopic studies, a new class of organometallic compounds of zinc with novel Zn_4N_8, Zn_4N_6O and $Zn_4N_4O_2$ cage struc-

Table 4. Selected bond lengths [Å] and angles [°] for one of the two independent molecules of [$(MeZn)_4(NHNMe_2)_2(OEt)_2$] (**7**) and of [$(EtZn)_4(NHNMe_2)_2(OEt)_2$] (**8**) as determined by X-ray crystallography.

[$(MeZn)_4(NHNMe_2)_2(OEt)_2$] (**7**)		[$(EtZn)_4(NHNMe_2)_2(OEt)_2$] (**8**)	
Zn(1)–C(11)	1.982(8)	Zn(1A)–C(11A)	1.984(13)
Zn(1)–N(11)	2.076 (6)	Zn(1A)–N(21A)	2.086(9)
Zn(1)–N(21)	2.062(6)	Zn(1A)–N(11A)	2.065(10)
Zn(1)–O(31)	2.109(5)	Zn(1A)–O(1A)	2.110(10)
Zn(2)–C(21)	1.983(9)	Zn(2A)–C(21A)	2.005(16)
Zn(2)–N(11)	2.029(6)	Zn(2A)–N(21A)	2.021(10)
Zn(2)–O(41)	2.088(5)	Zn(2A)–O(4A)	2.057(10)
Zn(4)–C(41)	1.970(9)	Zn(4A)–C(41A)	1.940(3)
Zn(4)–N(12)	2.100(6)	Zn(4A)–N(22A)	2.099(12)
Zn(4)–O(31)	2.047(6)	Zn(4A)–O(1A)	2.027(9)
Zn(4)–O(41)	2.068(5)	Zn(4A)–O(4A)	2.048(11)
N(11)–N(12)	1.473(8)	N(21A)–N(22A)	1.453(14)
C(11)-Zn(1)-N(21)	130.3(4)	C(11A)-Zn(1A)-N(11A)	127.4(6)
C(11)-Zn(1)-N(11)	121.8(4)	C(11A)-Zn(1A)-N(21A)	124.1(5)
N(21)-Zn(1)-N(11)	96.0(2)	N(11A)-Zn(1A)-N(21A)	96.7(4)
C(11)-Zn(1)-O(31)	119.0(4)	C(11A)-Zn(1A)-O(1A)	121.1(6)
N(21)-Zn(1)-O(31)	93.5(2)	N(11A)-Zn(1A)-O(1A)	83.9(5)
N(11)-Zn(1)-O(31)	93.5(2)	N(21A)-Zn(1A)-O(1A)	92.5(4)
N(11)-Zn(2)-O(41)	90.5(2)	N(21A)-Zn(2A)-O(4A)	91.0(4)
O(31)-Zn(4)-O(41)	85.9(2)	O(1A)-Zn(4A)-O(4A)	85.9(4)
O(31)-Zn(4)-N(12)	94.7(2)	O(1A)-Zn(4A)-N(22A)	94.0(4)
O(41)-Zn(4)-N(12)	94.1(2)	O(4A)-Zn(4A)-N(22A)	93.5(4)
N(12)-N(11)-Zn(2)	111.2(4)	N(22A)-N(21A)-Zn(2A)	111.2(7)

tures. The parent zinc hydrazides are accessible by the reactions of zinc alkyls with hydrazine. Increasing the hydrazine/zinc alkyl ratio from 1:1 to 2:1 or 3:1 has no effect on the stoichiometry of the resulting zinc hydrazide aggregates. The zinc hydrazide/alkoxide and zinc hydrazide/hydroxide clusters are accessible via two different synthetic pathways. In one, the target compounds are prepared by the reaction of zinc hydrazide with alkoxides. In the other, the zinc hydrazide/alkoxides are prepared in "one-pot" syntheses, the reaction of zinc alkyl with mixtures of hydrazine and alkoxide. The reaction conditions have to be optimised in each case and generally involve the application of excess hydrazine.

These new tetrazinc clusters allow the Zn/N/O ratio in the molecules to be changed from 4:8:0 to 4:6:1 to 4:4:2. The clusters comprise new structural motifs for completely asymmetric Zn_4N_8 cages, C_3-symmetric Zn_4N_6O cages and asymmetric $Zn_4N_4O_2$ cages.

Further investigations into new substitution patterns, involvement of other OH-functional compounds in the alcoholysis or one-pot reactions and new aggregation modes are in progress as well as thermal decomposition experiments of these cluster compounds under different conditions.

Experimental Section

General considerations: All manipulations of air-sensitive compounds were carried out under a purified nitrogen atmosphere with standard Schlenk and high-vacuum techniques using double manifolds, or under argon in a glovebox. Solvents were purified and dried by standard methods immediately before use. *N*,*N*-Dimethylhydrazine was purchased from Aldrich Chemical Company and dried by distillation from CaH_2 under dry nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 300, 400, or 500, or a Varian Unity Plus 600, spectrometer in $CDCl_3$ as solvent, dried over activated molecular sieves. ^{1}H and ^{13}C assignments were confirmed when necessary with the use of two-dimensional ^{1}H–^{1}H and ^{13}C–^{1}H correlation NMR experiments. All spectra were referenced internally to residual protiosolvent (^{1}H) or solvent (^{13}C) resonances. A Nonius Kappa-CCD X-ray diffractometer (λ = 0.71073 Å) was used to collect the scattering intensities for single-crystal structure determination. IR spectra were measured with a Bruker IFS (103 V) instrument using KBr pellets prepared in a glovebox.

General procedure for [$(MeZn)_4(NHNMe_2)_4$] (1) and [$(EtZn)_4(NHNMe_2)_4$] (2) synthesis: R_2Zn (R = Me, Et) (10 mL of a 2 M solution in *n*-hexane/toluene; 20 mmol) was added dropwise via a syringe to a stirred solution of H_2NNMe_2 (2.30 mL, 30 mmol) in *n*-hexane (20 mL) at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred for 6 h. After removal of the solvent under reduced pressure, the resulting residue was dissolved in *n*-hexane and filtered. The clear, colourless filtrate, when stored at −10 °C, afforded colourless crystals of **1** and **2**.

*Data for **1***: Yield: 65 % (1.81 g, 3.24 mmol); m.p. >300 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −1.10 (s, 8H; $\mathrm{ZnC}H_3$), −1.00 (s, 4H; $ZnCH_3$), 2.02 (s, 1H; N–H), 2.07 (s, 3H; N–H), 2.22–2.74 ppm (m, 24H; $N(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = −18.57, −16.72, −14.87, −11.53 ($ZnCH_3$), 53.03, 53.32, 54.30, 54.50, 54.74, 55.25, 56.62, 57.23 ppm (NCH_3); EI-MS: *m*/*z* (%): 543 (36) [$M^+ - CH_3$]; IR (KBr film): $\tilde{\nu}$ = 3144, 3177 (N–H) cm^{-1}; elemental analysis (%) calcd for $C_{12}H_{40}N_8Zn_4$: C 25.83, H 7.22, N 20.08; found: C 25.15, H 6.98, N 18.17.

*Data for **2***: Yield: 75 % (2.3 g, 3.74 mmol); m.p. 202–203 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$): δ = −0.27 (q, *J* = 8.1 Hz, 2H; $ZnCH_2$), −0.23 to −0.17 (m, 4H; $ZnCH_2$), −0.14 (q, *J* = 8.1 Hz, 2H; $ZnCH_2$), 1.11–1.18 (m, 12H; $\mathrm{ZnCH_2C}H_3$), 2.04 (s, 1H; N–*H*), 2.09 (s, 2H; N–H), 2.21 (s, 1H; N–H), 2.32–2.73 ppm (m, 24H; $N(CH_3)_2$); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ = −3.32, −0.57, −0.48, 1.84 ($ZnCH_2$), 13.93, 14.04, 14.07 ($ZnCH_2CH_3$), 53.51, 54.48, 54.83, 55.30, 55.90, 56.56, 56.76, 57.52 ppm (NCH_3); EI-MS: *m*/*z* (%): 585 (100) [$M^+ - C_2H_5$]; IR (KBr film): $\tilde{\nu}$ = 3150, 3175 (N–H) cm^{-1}; elemental analysis (%) calcd for $C_{16}H_{48}N_8Zn_4$: C 31.29, H 7.88, N 18.24; found: C 31.18, H 7.97, N 17.93.

General procedure for [$(MeZn)_4(OH)(NHNMe_2)_3$] (3) and [$(EtZn)_4(OH)(NHNMe_2)_3$] (4) synthesis: E_2Zn (E = Me, Et) (5 mL, 2 M, in *n*-hexane/toluene; 10 mmol) was added dropwise via a syringe to a stirred solution of H_2NNMe_2 (0.6 mL, 7.83 mmol) in *n*-hexane (10 mL) at 0 °C. Water (0.07 mL, 3.88 mmol) was added dropwise via a syringe. The reaction mixture was warmed gradually to room temperature and stirred for 6 h. After removal of the solvent under reduced pressure, the resulting residue was dissolved in *n*-hexane and filtered. The clear, colourless filtrate, when stored at −10 °C, afforded colourless crystals of **3** and **4**.

*Data for **3***: Yield: 40 % (516 mg, 1.0 mmol); m.p. >300 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −1.11 (s, 3H; $ZnCH_3$), −1.00 (s, 9H; $ZnCH_3$), 2.06 (s, 3H; N–H), 2.44 (s, 9H; $N(CH_3)_2$), 2.61 ppm (s, 9H; $N(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = −16.72, −12.47 ($ZnCH_3$), 53.05, 54.51 ppm (NCH_3); EI-MS: *m*/*z* (%): 501 (70) [$M^+ - CH_3$]; IR (KBr film): $\tilde{\nu}$ = 3189 (N–H), 3606 (O–H) cm^{-1}.

*Data for **4***: Yield: 49 % (700 mg, 1.22 mmol); m.p. >300 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$): δ = −0.26 (q, *J* = 8.1 Hz, 2H; $ZnCH_2$), −0.05 (q, *J* = 8.1 Hz, 6H; $\mathrm{ZnC}H_2$), 1.12 (t, *J* = 8.1 Hz, 3H; $\mathrm{ZnCH_2C}H_3$), 1.16 (t, *J* = 8.1 Hz, 9H; $\mathrm{ZnCH_2C}H_3$), 2.08 (s, 3H; N–H), 2.42 (s, 9H; $N(CH_3)_2$), 2.63 ppm (s, 9H; $N(CH_3)_2$); $^{13}C\{^1H\}$ NMR (150.8 MHz, $CDCl_3$): δ = −2.17, −1.08 ($ZnCH_2$), 13.45, 14.00 ($ZnCH_2CH_3$), 53.27, 54.66 ppm (NCH_3); EI-MS: *m*/*z* (%): 543 (44) [$M^+ - C_2H_5$]; IR (KBr film): $\tilde{\nu}$ = 3186 (N–H), 3566 (O–H) cm^{-1}.

General procedure for [$(EtZn)_4(OMe)(NHNMe_2)_3$] (5) and [$(EtZn)_4(OEt)(NHNMe_2)_3$] (6) synthesis: Under an atmosphere of dry nitrogen, a solution of [$(EtZn)_4(NHNMe_2)_4$] (615 mg, 1.00 mmol) in *n*-hexane (20 mL) was cooled to 0 °C. MeOH (0.04 mL, 0.99 mmol) or EtOH (0.06 mL, 1.03 mmol) was added dropwise via a syringe. The reaction mixture was warmed gradually to room temperature and stirred for 6 h.

After removal of the solvent under reduced pressure, the resulting residue was dissolved in *n*-hexane and filtered. The clear, colourless filtrate was stored at −10 °C and afforded colourless crystals of **5** and **6** after several days.

Data for **5**: Yield: 45 % (264 mg, 0.45 mmol); m.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.30 (q, J = 8.2 Hz, 2 H; $ZnC\mathit{H}_2CH_3$), −0.03 (q, J = 8.2 Hz, 6 H; $ZnC\mathit{H}_2CH_3$), 1.09 (t, J = 8.2 Hz, 3 H; $ZnC\mathit{H}_2CH_3$), 1.17 (t, J = 8.2 Hz, 9 H; $ZnC\mathit{H}_2CH_3$), 2.05 (s, 3 H; N−H), 2.39 (s, 9 H; $N(CH_3)_2$), 2.63 (s, 9 H; $N(C\mathit{H}_3)_2$), 3.59 ppm (s, 3 H; OCH_3); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ = −2.56, −1.19 ($ZnCH_2$), 13.66, 18.28 ($ZnCH_2\mathit{C}H_3$), 51.75 ($O\mathit{C}H_3$), 53.49, 55.12 ($N\mathit{C}H_3$); EI-MS: *m*/*z* (%): 557 (100) $[M^+-C_2H_5]$; IR (KBr film): $\tilde{\nu}$=3235 (N−H) cm^{-1}.

Data for **6**: Yield: 35 % (212 mg, 0.35 mmol); m.p. >300 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.29 (q, J = 8.2 Hz, 2 H; $ZnC\mathit{H}_2CH_3$), 0.00 (q, J = 8.2 Hz, 4 H; $ZnC\mathit{H}_2CH_3$), 0.01 (q, J = 8.2 Hz, 2 H; $ZnC\mathit{H}_2CH_3$), 1.10 (t, J = 8.2 Hz, 3 H; $ZnC\mathit{H}_2CH_3$), 1.16 (t, J = 8.2 Hz, 9 H; $ZnC\mathit{H}_2CH_3$), 1.31 (t, J = 7.0 Hz, 3 H; $OC\mathit{H}_2CH_3$), 2.05 (s, 3 H; N−H), 2.39 (s, 9 H; $N(CH_3)_2$), 2.63 (s, 9 H; $N(CH_3)_2$), 3.84 ppm (q, J = 7.0 Hz, 3 H; OCH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = −0.61, 1.24 ($Zn\mathit{C}H_2$), 13.64, 14.23 ($ZnCH_2\mathit{C}H_3$), 20.38 ($OCH_2\mathit{C}H_3$), 53.63, 54.93 (NCH_3), 65.40 ppm ($O\mathit{C}H_2CH_3$); EI-MS: *m*/*z* (%): 571 (100) $[M^+-C_2H_5]$; IR (KBr film): $\tilde{\nu}$= 3180 (N−H) cm^{-1}.

General procedure for $[(MeZn)_4(NHNMe_2)_2(OEt)_2]$ (7) and $[(EtZn)_4(NHNMe_2)_2(OEt)_2]$ (8) synthesis: R_2Zn (R = Me, Et) (5 mL, 2 M, in *n*-hexane/toluene; 10 mmol) was added dropwise via a syringe to a stirred solution of H_2NNMe_2 (0.4 mL, 5.22 mmol) and EtOH (0.25 mL, 5.60 mmol) in *n*-hexane (10 mL) at 0 °C. The reaction mixture was warmed gradually to room temperature and stirred for 4 h. After removal of the solvent under reduced pressure, the resulting residue was dissolved in *n*-hexane and filtered. The clear, colourless filtrate was stored at −26 °C, to afford colourless crystals of **7** and **8**.

Data for **7**: Yield: 45 % (596 mg, 1.12 mmol); m.p. >300 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.98 (s, 3 H; $ZnCH_3$), −0.94 (s, 3 H; $ZnCH_3$), −0.86 (s, 3 H; $ZnC\mathit{H}_3$), −0.81 (s, 3 H; $ZnCH_3$), 1.18 (t, J = 7.0 Hz, 3 H; $OCH_2C\mathit{H}_3$), 1.28 (t, J = 7.0 Hz, 3 H; $OCH_2C\mathit{H}_3$), 2.08, 2.15 (s, 2 H; N−H), 2.34–2.69 (m, 12 H; $N(CH_3)_2$), 3.75 (q, J = 7.0 Hz, 2 H; $OC\mathit{H}_2CH_3$), 3.86 ppm (q, J = 7.0 Hz, 2 H; $OC\mathit{H}_2CH_3$); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = −19.60, −16.47, −15.84, −14.46 ($Zn\mathit{C}H_3$), 20.30, 22.63 ($OCH_2\mathit{C}H_3$), 53.34, 53.51, 54.04, 54.15 ($N\mathit{C}H_3$), 63.05, 63.72 ppm ($O\mathit{C}H_2CH_3$); EI-MS: *m*/*z* (%): 501 (40) $[M^+-C_2H_5]$; 375 (56) $[M^+-C_2H_5-MeZnOEt]$; IR (KBr film): $\tilde{\nu}$= 3178 (N−H) cm^{-1}.

Data for **8**: Yield: 55 % (805 mg, 1.37 mmol); m.p. >300 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.07 (q, J = 8.3 Hz, 2 H; $ZnC\mathit{H}_2CH_3$), −0.01 (q, J = 8.3 Hz, 2 H; $ZnC\mathit{H}_2CH_3$), −0.09–0.18 (m, 4 H; $ZnC\mathit{H}_2CH_3$), 1.13 (t, J = 8.2 Hz, 3 H; $ZnC\mathit{H}_2CH_3$), 1.17 (t, J = 8.2 Hz, 3 H; $ZnC\mathit{H}_2CH_3$), 1.20 (t, J = 8.2 Hz, 6 H; $ZnC\mathit{H}_2CH_3$), 1.22 (t, J = 7.0 Hz, 3 H; $OCH_2C\mathit{H}_3$), 1.31 (t, J = 7.0 Hz, 3 H; $OCH_2C\mathit{H}_3$), 2.13, 2.16 (s, 2 H; N−*H*), 2.33–2.68 (m, 12 H; $N(C\mathit{H}_3)_2$), 3.79 (q, J = 7.0 Hz, 2 H; $OC\mathit{H}_2CH_3$), 3.90 ppm (q, J = 7.0 Hz, 2 H; $OC\mathit{H}_2CH_3$); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = −3.93, −1.79, −1.53, −0.50 ($Zn\mathit{C}H_2CH_3$), 12.71, 12.95, 13.34, 13.39 ($ZnCH_2CH_3$), 20.50, 20.56 ($OCH_2\mathit{C}H_3$), 53.45, 53.65, 54.23, 54.46 ($N\mathit{C}H_3$), 62.79, 63.94 ppm ($O\mathit{C}H_2CH_3$); EI-MS: *m*/*z* (%): 557 (100) $[M^+-C_2H_5]$; 417 (61) $[M^+-C_2H_5-EtZnOEt]$; IR (KBr film): $\tilde{\nu}$= 3181 (N−H) cm^{-1}; elemental analysis (%) calcd for $C_{16}H_{44}N_4O_2Zn_4$: C 32.79, H 7.57, N 9.56; found: C 31.83, H 7.40, N 9.47.

Crystal structures: Crystals of the compounds **2**, **3**, **4**, **5**, **7** and **8** were selected and prepared under perfluoropolyether and mounted in a drop of it onto the tip of a glass fibre on the goniometer head of a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined with the full-matrix least-squares procedure (SHELXTL[21]) against F^2. For details of the crystal data and refinements, see Table 5.

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Table 5. Crystal and refinement data for **2**, **3**, **4**, **5**, **7** and **8**.

	2	**3**	**4**	**5**	**7**	**8**
formula	$C_{16}H_{48}N_8Zn_4$	$C_{10}H_{34}N_6OZn_4$	$C_{14}H_{42}N_6OZn_4$	$C_{15}H_{44}N_6OZn_4$	$C_{12}H_{36}N_4O_2Zn_4$	$C_{16}H_{44}N_4O_2Zn_4$
M_r	614.12	515.91	572.02	586.04	529.93	586.03
crystal system	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
a [Å]	11.615(1)	9.305(1)	18.149(1)	14.484(1)	17.362(1)	17.713(1)
b [Å]	14.685(1)	9.999(1)	9.409(1)	21.258(1)	17.026(1)	17.840(1)
c [Å]	16.246(1)	12.997(1)	29.075(1)	17.326(1)	16.908(1)	17.550(1)
α [°]	90	69.21(1)	90	90	90	90
β [°]	101.45(1)	89.91(1)	90	101.78(1)	112.08(1)	107.57(1)
γ [°]	90	70.06(1)	90	90	90	90
V [Å^3]	2715.9(3)	1052.8(2)	4965.0(6)	5222.3(5)	4631.5(5)	5287.1(5)
T [°C]	−75	−75	−75	−75	−75	−75
space group	$P2_1/n$	$P\bar{1}$	$Pca2_1$	$P2_1/n$	$P2_1/c$	$P2_1/c$
Z	4	2	8	8	8	8
ρ_{calcd} [g cm^{-3}]	1.502	1.627	1.530	1.491	1.520	1.472
crystal size [mm^3]	0.45 × 0.10 × 0.05	0.55 × 0.40 × 0.20	0.25 × 0.15 × 0.10	0.30 × 0.15 × 0.05	0.25 × 0.15 × 0.10	0.50 × 0.50 × 0.30
ext. coeff.	–	0.0053(10)	–	–	–	–
μ [mm^{-1}]	3.507	4.507	3.831	3.644	4.101	3.600
refl.$_{collected}$	19761	9557	30284	42147	26400	49013
refl.$_{unique}$	5574	5045	10498	12405	8155	6894
R_{int}	0.053	0.034	0.0753	0.0690	0.0876	0.057
R_1/wR_2 ($I>2\sigma(I)$)	0.0465/0.1189	0.0291/0.0713	0.0511/0.1068	0.0520/0.1121	0.0622/0.1429	0.0904/0.2410
R_1/wR_2 (all data)	0.0734/0.1321	0.0348/0.0744	0.0923/0.1194	0.1127/0.1320	0.1465/0.1724	0.1530/0.2944
$\Delta\rho_{fin}$ [e Å^{-3}]	1.25/−0.58	0.67/−0.64	0.57/−0.46	0.88/−0.75	2.33/−1.24	2.44/−0.67
CCDC number[a]	262623	262624	273712	273713	273714	273715

[a] 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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