

“Isomerism” of Coordination Modes and Numbers in Pentanuclear Organozinc Hydroxylamides: An Exercise in Subtle Substituent Size Effects

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Dedicated to Prof. Gerhard Erker on the occasion of his 60th birthday

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The first organometallic zinc hydroxylamides $[\text{Zn}(\text{RZn})_4(\text{ONMe}_2)_6]$ (**1**: R = Me; **2**: R = *i*Pr) and $[\text{Zn}(\text{EtZn})_4(\text{ONe}_2)_6]$ (**3**) have been prepared by alkane elimination from dialkylzinc solutions upon treatment with *N,N*-dialkylhydroxylamines. The molecular structures of **1** and **2** reveal that a subtle change in the constitution of the aggregates can make a striking difference. By the simple exchange of the MeZn^+ groups with *i*PrZn⁺ groups, the coordination number of the central Zn^{2+} nucleus increases from four (**1**) to six (**2**). The two cluster types are unprecedented in both hydroxylamine and organometallic chemistry. Compounds **1** and **3** adopt a doubly bridged fenestrane-like $\text{Zn}_5\text{N}_6\text{O}_6$ core with two dangling NR_2 moieties, whereas *i*PrZn species **2** comprises an octahedroid backbone with all donor atoms attached to the

five Zn nuclei with the maintenance of the same heteroatom composition as **1** and **3**. Variable-temperature ^{13}C NMR experiments of all-ethyl cluster **3** reveal that the R_2NO^- ligands rapidly exchange between the RZn^+ and Zn^{2+} cations. This process is rationalised by a plausible model which also points out that the core structure of **3** could be an intermediate motif in the observed heteroatom connectivity exchange. In line with this, computational investigations reveal that both skeletons are very similar in energy. In sum, the coordination flexibility of the hydroxylamide ligand makes this group of organometallic zinc complexes a highly dynamic family of cluster compounds.

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Introduction

Compared to organometallics of the trivalent group 13 elements, zinc requires further contact to a donor atom to reach coordination number (CN) four because of its divalent nature. In metal alkoxide/aryloxide chemistry,^[1] an increase in aggregate dimensionality is already well established [compare the Al_2O_2 ring $\{(\text{Me}_2\text{Al})[\text{O}(2,6\text{-}i\text{Pr}_2\text{-C}_6\text{H}_3)]_2\}_2$ ^[2] with the “double cube” $[(\text{MeZn})_3(\text{OMe})_4]\text{Zn}$ ^[3] (CN = 4, 6)].^[4] The highly diverse chemistry of the O–N double-donor array (hydroxylamines or oximes) provides a plethora of aggregation motifs, for example in group 13 complexes,^[5–9] and ought to be transferable to zinc for the exploration of similar extensions {compare the six-membered ring dimer $[(\text{Me}_2\text{Al})(\text{ON}=\text{CMe}_2)]_2$ ^[5a,5b] with the tetrahedroid oximate $[(\text{MeZn})(\text{ON}=\text{CMe}_2)]_4$ ^[10] (CN = 4)}.

The high coordination flexibility of the hydroxylamide ligands that is demonstrated in Al and Ga organometallics (e.g. in the readily fluctuating tetracyclic Al_3 cluster $\{[(\text{Me}_2\text{Al})[\text{ON}(\text{Me})_2\text{CH}_2]_2(\text{AlMe})]^{[6]}\}$ can be expected by hypothesis to allow for the construction of highly dynamic Zn-based multinuclear cluster compounds. Zinc, on its own accord, has a very rich alkoxide chemistry.^[1,3] However, hydroxylamide derivatives of divalent metals are rather poorly understood and encompass merely inorganic coordination compounds of zinc^[11] {e.g. $[(\text{H}_2\text{NOH})_2\text{ZnCl}_2]$, Crismer’s salt^{[12]}}}, but organometallic examples are completely unknown.

We report herein the initial evidence to support the above hypothesis. The reaction of *N,N*-dialkylhydroxylamines Me_2NOH or Et_2NOH with binary zinc alkyls affords three pentanuclear organozinc cluster compounds: $[\text{Zn}(\text{RZn})_4(\text{ONMe}_2)_6]$ (**1**: R = Me; **2**: R = *i*Pr) and $[\text{Zn}(\text{EtZn})_4(\text{ONe}_2)_6]$ (**3**, vide infra).

Results and Discussion

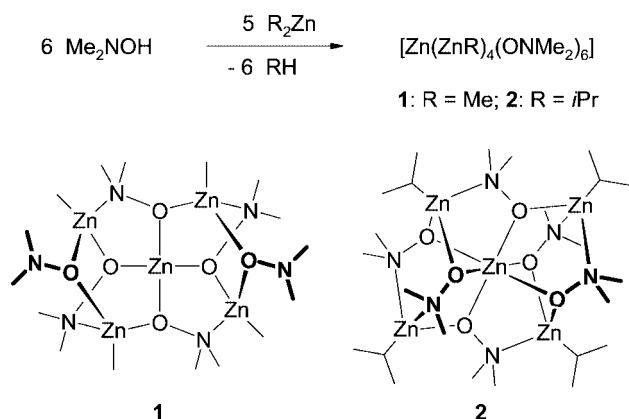
With the focus on compounds **1** and **2** (Scheme 1), it is elegantly revealed that the highly flexible coordinating O–N ligands allow Zn atoms to adopt a CN > 4. This

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stands in contrast to the isoelectronically related organozinc hydrazides (N–N double-donor), where zinc is exclusively tetracoordinate.^[13]



Scheme 1.

Though the formulae of **1** and **2** (apart from the alkyl groups on Zn) are identical, their three-dimensional coordination frameworks differ markedly. The all-methyl cluster $[\text{Zn}(\text{MeZn})_4(\text{ONMe}_2)_6]$ (**1**) adopts a fenestrane-like motif, as determined by X-ray diffraction analysis (Figure 1).^[14] Four O–N moieties coordinate around the central “inorganic” Zn^{2+} ion by their oxygen atoms and are themselves interconnected by RZn^+ units via O–Zn–N linkages. The resulting dicationic heterofenestrane $\{[\text{Zn}(\text{ONMe}_2)_4(\text{ZnMe})_4]^{2+}\}$ is then charge-compensated by two anionic μ^2 -O-bridging Me_2NO^- ligands. If the latter are neglected, the core of **1** is reminiscent of a handful of known complexes (e.g. in bioinorganics),^[15] but those complexes exhibit solely square-planar coordinated central metal ions and have no

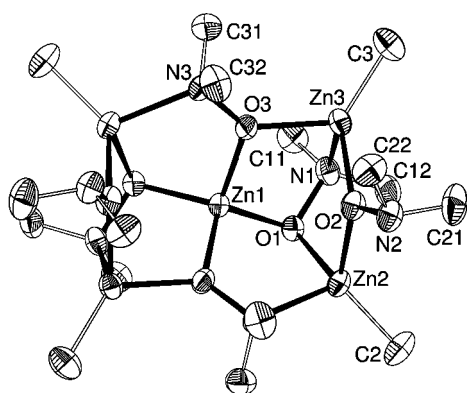


Figure 1. Crystal structure of **1** (thermal ellipsoids at 50% probability; hydrogen atoms are omitted; symmetry transformations used to generate equivalent atoms: $-x+1, y, -z+3/2$). Selected distances and angles [Å/°]: Zn1–O3 1.923(3), Zn2–O1 2.100(2), Zn3–N1 2.175(3), O3–N3 1.435(4), Zn2–C2 1.966(4), N3–C32 1.464(5); O1–Zn2–O2 86.8(1), O1–Zn1–O1' 132.5(1), O3–Zn3–N1 85.8(1), O2–Zn2–N3' 103.5(1), Zn1–O1–Zn2 100.0(1), Zn2–O2–Zn3 121.9(1), Zn1–O1–N1 107.9(2), Zn3–O2–N2 123.8(2), Zn3–N1–O1 107.3(2), Zn2–N3'–O3' 111.6(2), Zn2–N3'–C32' 110.2(3), O2–N2–C21 107.2(3), C21–N2–C22 109.8(4).

M–C bonds. The aggregation motif of **1** (all Zn atoms: CN = 4) is unprecedented in both hydroxylamine and organometallic chemistry.

With a subtle size change of the alkyl group at zinc (from Me to *i*Pr), the core structure of the aggregate completely shifts as revealed by the crystal structure of ether solvate **2**·OEt₂ (Figure 2).^[14] In this cluster, the ether molecule fills a void but does not contact any of the Zn atoms. The hydroxylamide cluster $[\text{Zn}(\text{ONMe}_2)_6(\text{Zn}i\text{Pr})_4]$ (**2**) adopts an octahedral-based structure with all six O–N ligands O-bound to the central Zn^{2+} (CN = 6). Charge compensation of this $[\text{Zn}(\text{ONMe}_2)_6]^{4+}$ fragment is achieved by four *i*PrZn⁺ groups, which bind to the six O–N units either in an N,O,O- or in an N,N,O mode. Because all of the O and N atoms are now coordinated to Zn, this contrasts the situation in **1** which has two dangling NMe₂ groups – one key feature of the observed coordination “isomerism”. Consequently, cluster **2** is one of the limited examples of Zn species that exhibit mixed CNs, whether in organometallic^[1,3] or in inorganic chemistry.^[16]

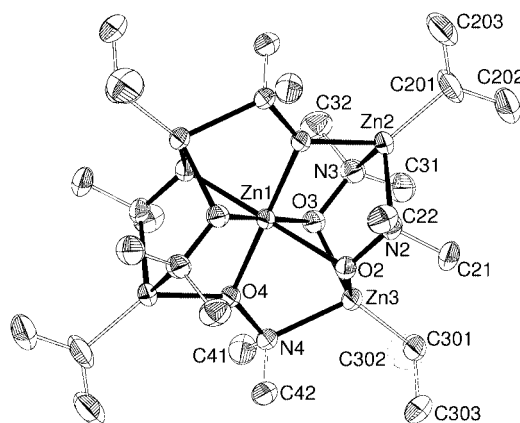
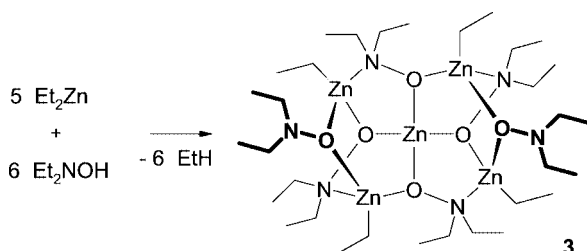


Figure 2. Solid-state structure of **2** in a crystal of the composition **2**·OEt₂ (thermal ellipsoids at 50% probability; hydrogen atoms and the Et₂O solvate molecule are omitted; symmetry transformations used to generate equivalent atoms: $-x+1, -y+2, -z$). Selected distances and angles [Å/°]: Zn2–O4' 1.974(2), Zn1–O2 2.205(2), Zn3–N4 2.135(2), O4–N4 1.433(2), Zn2–C201 1.987(3), N3–C32 1.467(3); O2–Zn1–O3 78.0(1), O2–Zn1–O3' 102.0(1), O4'–Zn2–N12 85.2(1), O3–Zn3–N4 106.0(1), Zn1–O12–Zn3 102.1(1), Zn2–O3–Zn3 119.3(1), Zn3–O3–N3 108.5(1), Zn2–O3–N3 122.8(1), Zn3–N4–O4 112.2(2), Zn3–N4–C41 109.0(2), O3–N3–C33 106.9(2), C41–N4–C43 110.8(3).

Although the structures of **1** and **2** are not the same, their core compositions are, and thus, the question arises whether a pathway for the interconversion between the two cluster types exists. VT-NMR spectroscopy sheds some light onto this and onto the molecular dynamics of the aggregates. Between 300 and 200 K, the ¹H NMR spectra of **1** show some signal broadening but no substantial change to indicate structural variations; the ¹³C NMR spectra give a similar picture. A drawback to these measurements is the limited solubility of **1** especially at low temperatures, which is most probably due to its minimal alkyl periphery.

Fortunately, the all-ethyl analogue $[\text{Zn}(\text{EtZn})_4(\text{ONEt}_2)_6]$ (**3**, Scheme 2) is much more soluble and represents an exquisite VT-NMR substitute for all-methyl cluster **1** because it adopts the same core motif (Figure 3). Furthermore, the fact that **1** and **3** exhibit the same coordination framework underlines that the structural differences between **1** and **2** cannot be accounted for merely by means of the steric congestion of the “organic sphere” about the $\text{Zn}_5\text{N}_6\text{O}_6$ heteroatom core. The number of carbon atoms in that sphere doubles from 16 (compound **1**) to 32 (compound **3**) without any effect on the aggregation motif. Exchange of the MeZn^+ groups (compound **1**) by $i\text{PrZn}^+$ groups (compound **2**) increases that number only by 8 (from 16 to 24). A simple focus on group sizes – though obvious when only differences between **1** and **2** are examined based on the literature findings of EtZn boryloxides^[17] or Stephan’s bulky Me_2Al aryloxide^[2] (compared to “normal” Al-O organyls with $\text{CN} > 4$ ^[1]) – is not a definite reason for the varied CN of the present organozinc hydroxylamides. In fact, if bulkiness of the group had an influence on the CN of the central “inorganic” Zn^{2+} nucleus, the opposite trend in the CN would



Scheme 2.

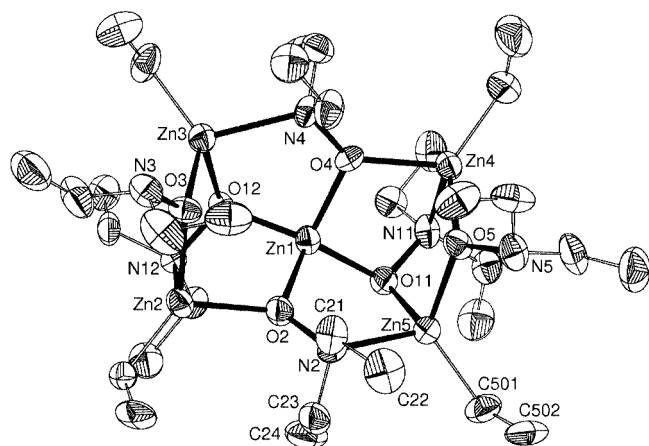


Figure 3. Crystal structure of **3** (thermal ellipsoids at 50% probability; hydrogen atoms and the disorder of the ethyl group at $\text{Zn}2$ are omitted). Selected distances and angles [$\text{\AA}/^\circ$]: $\text{Zn}1\text{--O}11$ 1.944(7), $\text{Zn}2\text{--O}3$ 2.041(7), $\text{Zn}4\text{--N}11$ 2.186(9), $\text{O}2\text{--N}2$ 1.444(11), $\text{Zn}5\text{--C}501$ 1.972(12), $\text{N}2\text{--C}23$ 1.461(15); $\text{O}5\text{--Zn}5\text{--O}11$ 88.7(3), $\text{O}11\text{--Zn}1\text{--O}12$ 139.7(3), $\text{O}2\text{--Zn}2\text{--N}12$ 86.2(3), $\text{O}3\text{--Zn}3\text{--N}4$ 107.8(3), $\text{Zn}1\text{--O}11\text{--Zn}5$ 102.3(3), $\text{Zn}4\text{--O}5\text{--Zn}5$ 117.7(3), $\text{Zn}1\text{--O}12\text{--N}12$ 109.7(5), $\text{Zn}4\text{--O}5\text{--N}5$ 121.9(6), $\text{Zn}4\text{--N}11\text{--O}11$ 104.5(5), $\text{Zn}5\text{--N}2\text{--O}2$ 112.9(6), $\text{Zn}5\text{--N}2\text{--C}21$ 112.6(7), $\text{O}2\text{--N}2\text{--C}23$ 106.0(8), $\text{C}21\text{--N}2\text{--C}23$ 110.8(10).

be expected. The overall packing in the aggregation motif found for **2** is more compact than the one found for **1** and **3**.

The ^{13}C NMR spectrum of **3** at 298 K exhibits broad features for the nitrogen-bound ethyl substituents in the regions between ca. 50 and 60 ppm and between ca. 10 and 15 ppm (Figure 4). At 213 K however, all five resonances are well-resolved and observable. This is in accordance with a C_2 molecular symmetry with freely rotating O--N bonds to the dangling NEt_2 groups. The ethyl groups at zinc give two sets of sharp resonances at both low and ambient temperatures. Obviously, the R_2NO^- units in compounds **1** and **3** exchange between the five Zn nuclei in a highly fluxional manner.

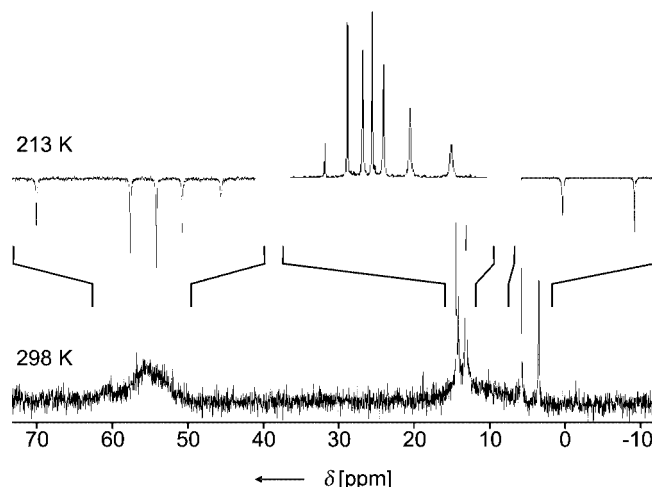


Figure 4. Details of the ^{13}C NMR spectra of $[\text{Zn}(\text{ZnEt})_4(\text{ONEt}_2)_6]$ (**3**) at 298 K (in $[\text{D}_6]\text{benzene}$) and at 213 K (in $[\text{D}_8]\text{toluene}$, DEPT 135 mode).

The ^1H NMR spectrum of **2** (Figure 5) displays one prominent resonance for the Me_2NO^- units at 300 K, which indicates an exchange on the NMR time scale comparable in magnitude to that found for the R_2NO^- units of **1** and **3**. At temperatures below 270 K, this peak splits into a complex set of signals of rather low resolution. Thus, a drop in the symmetry of the molecule below that of the crystalline state (C_2) can be assumed since the latter would require six chemically different N-Me groups. From the complexity of the NMR spectrum, the presence of more than one isomeric species in solution is reasonable. The two motifs found in the solid state for **1** and **2** are two likely possibilities.

The observed highly dynamic behaviour is consistent with rapidly isomerising aggregates. A plausible model is illustrated in Scheme 3a with the heteroatom core of **1**. The process by which this core is transformed into itself can be reasoned by the division of the process into four single steps.^[18,19] The first two steps involve the bond formation between the peripheral noncoordinated N atom and an RZn^+ group [colour code: green (1)]; in addition, there is a change in connectivity of the O atom of the hydroxylamide from a peripheral Zn atom to the central Zn atom [colour code: orange (2)]. The central Zn atom then becomes hexa-

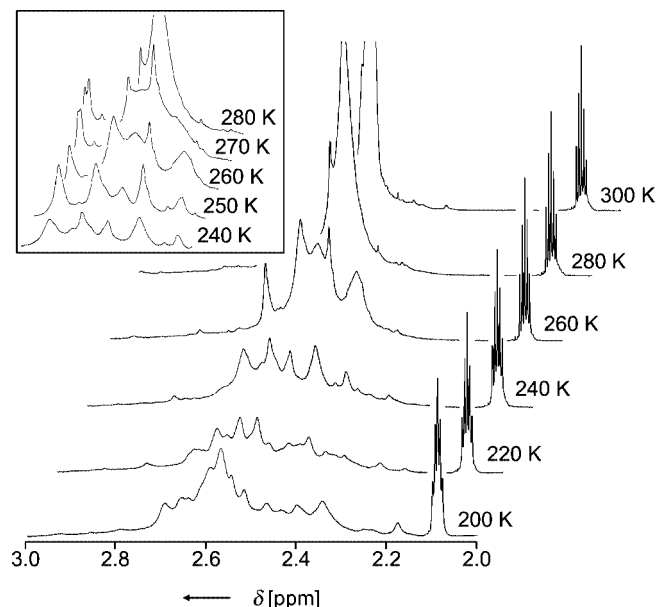
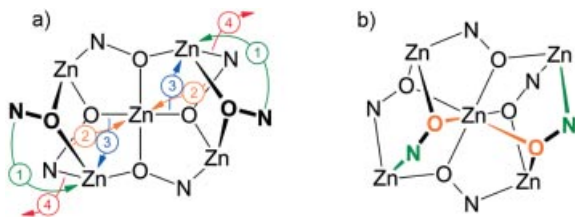


Figure 5. Variable-temperature ^1H NMR spectra of **2** (in $[\text{D}_8]\text{toluene}$) in the chemical shift region of the ONMe_2 moieties. For clarity, the highlighted temperature range around the coalescence point is provided in steps of 10 K.

coordinate, and this finalises the transformation of the core structure from the type adopted by compound **1** to that of **2** in the crystalline state.



Scheme 3. a) Plausible model for the fluctuation of the O–N ligands. The overall C_2 symmetry compels each step to occur twice. b) The isomeric heteroatom cluster core as found for **2** in the solid state – an “intermediate” of the periodical fluctuation.

Two further steps that are reverse in nature to the preceding two allow the ligands to rearrange about the RZn^+ and Zn^{2+} atoms to reconstruct the heteroatom connectivity pattern as found in the solid state of **1** {the O atom of one O–N unit moves from the central Zn^{2+} nucleus to a peripheral RZn^+ group [colour code: blue (3)], and the N atom of the same O–N unit disconnects from the organozinc residue to become the dangling NR_2 group [colour code: red (4)]}.

In order to gain more detailed insight into the energetics of these systems, we calculated the energies of the two cluster types represented by **1** and **2** in the crystalline state for the most simple cases, all-methyl compound **1** and the MeZn^+ analogue of **2**, because both are unaffected by substituent conformations. The computations were carried out at the SCF/SV(P) and RI-BP/SV(P) levels of theory and reproduce the core structure parameters of the experimentally determined geometries well. At the SCF/SV(P) level, the aggregation adopted by compound **1** is slightly pre-

ferred by $5.4 \text{ kcal mol}^{-1}$. At the RI-BP/SV(P) level, the reverse was found; the structure of compound **2** was preferred with an energy difference of $1.2 \text{ kcal mol}^{-1}$.^[20]

The small differences in the theoretical calculations along with the temperature-dependent NMR studies reveal both aggregation motifs to be very comparable in energy. This explains the sensitivity of the observed aggregation and coordination modes on small substituent effects and the highly dynamic behaviour of the species. Thus, pentanuclear organozinc hydroxylamides **1–3** disclose for the first time that a metal can be flexibly coordinated by O–N ligands not only in terms of coordination modes but also numbers. On the basis of the experimental findings and the unique ability of the hydroxylamide ligand to be flexibly coordinating, this group of organometallic zinc complexes forms a highly dynamic family of cluster compounds.

Experimental Section

CAUTION: Pure zinc organyls may spontaneously ignite upon contact to air or moisture!

Materials and Methods: All manipulations were carried out under a dry nitrogen atmosphere with standard Schlenk and high-vacuum techniques with double manifolds or in a glove box (MBraun Lab Master 130) operated under an argon atmosphere. All solvents were purified by standard procedures immediately prior to use. Me_2Zn was obtained in its pure form by the fractional distillation of a commercial solution (2.0 M in toluene, Aldrich). Et_2Zn (Crompton GmbH, Bergkamen, Germany) was transferred into glassware in the glove box and used without further purification. $i\text{Pr}_2\text{Zn}$ was synthesised according to the literature^[21] and further purified by fractional condensation (removal of trace Et_2O from synthesis). It was stored in the dark at -78°C because it decomposes quite quickly upon exposure to light or ambient temperature. Me_2NOH was obtained from its hydrochloride salt (Aldrich) by treatment with excess NH_3 at -78°C and separated from the NH_4Cl residue by distillation.^[22] Et_2NOH (Aldrich) was purified by fractional distillation.

General Synthetic Protocol: R_2Zn ($\text{R} = \text{Me}, \text{Et}$ or $i\text{Pr}$) was condensed into a round-bottomed flask and then diluted with n -hexane to generate a ca. 1 M solution. With heavy stirring, a solution of Me_2NOH or Et_2NOH in THF (ca. 1 M) was slowly added at 0°C . The ice bath was removed, and the reaction mixture was stirred until gas evolution had ceased. All volatiles were evaporated under reduced pressure, and the colourless to light yellow viscous solid was extracted with n -hexane/ Et_2O and filtered. The resulting solution was carefully concentrated under reduced pressure and stored at -26°C (**1** and **3**) or -45°C (**2**) for several days to yield colourless crystals.

1: From Me_2Zn (15.8 mmol, 1.51 g) in n -hexane (15 mL), and Me_2NOH (19.0 mmol, 1.16 g, 1.30 mL) in THF (20 mL). Colourless cubes. Yield 1.35 g (1.80 mmol, 57%). ^1H NMR (200.1 MHz, $\text{C}_6\text{D}_5\text{CD}_3$): $\delta = -0.68$ to -0.15 (m, 12 H, $4 \times \text{ZnCH}_3$), 2.20–3.00 [m, very br., 36 H, $6 \times \text{N}(\text{CH}_3)_2$] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, $\text{C}_6\text{D}_5\text{CD}_3$): $\delta = 3.4, 5.7$ [$2 \times (2 \text{ C}, 2 \times \text{ZnCH}_3)$], 51–61 [very br., 12 C, $6 \times \text{N}(\text{CH}_3)_2$] ppm. $\text{C}_{16}\text{H}_{48}\text{N}_6\text{O}_6\text{Zn}_5$ (747.47): calcd. C 25.71, H 6.47, N 11.24; found C 25.34, H 6.32, N 11.12.

2: From $i\text{Pr}_2\text{Zn}$ (17.4 mmol, 2.64 g) in n -hexane (20 mL), and Me_2NOH (21.0 mmol, 1.28 g, 1.44 mL) in THF (20 mL). Colourless blocks. Yield 2.70 g (2.89 mmol, 83%). ^1H NMR (200.1 MHz,

CDCl_3): $\delta = 0.53$ [sept, $^3J_{\text{H,H}} = 7.5$ Hz, 4 H, $4 \times \text{ZnCH}(\text{CH}_3)_2$], 1.25 [d, $^3J_{\text{H,H}} = 7.5$ Hz, 24 H, $4 \times \text{ZnCH}(\text{CH}_3)_2$], 2.70 [s, 36 H, $6 \times \text{N}(\text{CH}_3)_2$] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, CDCl_3): $\delta = 11.6$ [4 C, $4 \times \text{ZnCH}(\text{CH}_3)_2$], 24.6 [8 C, $4 \times \text{ZnCH}(\text{CH}_3)_2$], 52.9 [12 C, $6 \times \text{N}(\text{CH}_3)_2$] ppm. MS (EI = 70 eV): m/z (%) = 648 (100) $\{M + H - (i\text{Pr}) - [(i\text{Pr})\text{ZnONMe}_2]\}^+$. $\text{C}_{24}\text{H}_{64}\text{N}_6\text{O}_6\text{Zn}_5$ (859.66): calcd. C 33.53, H 7.50, N 9.78; found C 33.24, H 7.43, N 9.65.

3: From Et_2Zn (19.0 mmol, 2.35 g) in *n*-hexane (20 mL), and $\text{Et}_2\text{-NOH}$ (22.9 mmol, 2.04 g, 2.35 mL) in THF (20 mL). Colourless blocks. Yield 3.36 g (3.46 mmol, 91%). ^1H NMR (599.8 MHz, 298 K, $\text{C}_6\text{D}_5\text{CD}_3$): $\delta = 0.37$, 0.37 [2 $\times$ (q, $^3J_{\text{H,H}} = 8.1$ Hz, 4 H, $2 \times \text{ZnCH}_2\text{CH}_3$)], ca. 0.85–1.25 [m, very br., 24 H, $4 \times \text{N}_{\text{coord}}(\text{CH}_2\text{CH}_3)_2$], 1.25 [t, $^3J_{\text{H,H}} = 7.2$ Hz, 12 H, $2 \times \text{N}_{\text{uncoord}}(\text{CH}_2\text{CH}_3)_2$], 1.51, 1.53 [2 $\times$ (t, $^3J_{\text{H,H}} = 8.1$ Hz, 6 H, $2 \times \text{ZnCH}_2\text{CH}_3$)], ca. 2.70–3.20 [m, very br., 24 H, $6 \times \text{N}(\text{CH}_2\text{-CH}_3)_2$] ppm. ^1H NMR (599.8 MHz, 213 K, $\text{C}_6\text{D}_5\text{CD}_3$): $\delta = 0.40$ –0.57 (m, 8 H, $4 \times \text{ZnCH}_2\text{CH}_3$), 0.75, 0.86 (2 $\times$ {t, br., $2 \times$ [3 H, $2 \times \text{N}_{\text{uncoord}}(\text{CH}_2\text{CH}_3)_2$]}), 1.18, 1.21, 1.27, 1.28 (4 $\times$ {t, br., $2 \times$ [3 H, $4 \times \text{N}_{\text{coord}}(\text{CH}_2\text{CH}_3)_2$]}), 1.67, 1.69 [2 $\times$ (t, br., $^3J_{\text{H,H}} = 8.3$ Hz, 6 H, $2 \times \text{ZnCH}_2\text{CH}_3$)], 2.27 (q, br., $^3J_{\text{H,H}} = 6.1$ Hz), 2.64 (q, br., 2.69 (q, br., $^3J_{\text{H,H}} = 6.3$ Hz), 2.81 (q, br., $^3J_{\text{H,H}} = 6.9$ Hz), 2.83 (q, br., $^3J_{\text{H,H}} = 6.9$ Hz), 2.88 (q, br., $^3J_{\text{H,H}} = 6.4$ Hz), 2.97 (q, br., $^3J_{\text{H,H}} = 6.2$ Hz), 3.08 (q, br.), 3.80 (m, br.) $\{8 \times (2 \text{ H, N}_{\text{coord}}\text{CH}_2\text{CH}_3); 1 \times [4 \times 2 \text{ H, } 2 \times \text{N}_{\text{uncoord}}(\text{CH}_2\text{CH}_3)_2]\}$ ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, 298 K, C_6D_6): $\delta = 3.4$, 5.7 [2 $\times$ (2 C, $2 \times \text{ZnCH}_2\text{CH}_3$)], ca. 11–17 [very br., 8 C, $4 \times \text{N}_{\text{coord}}(\text{CH}_2\text{CH}_3)_2$], 13.1 [4 C, $2 \times \text{N}_{\text{uncoord}}(\text{CH}_2\text{CH}_3)_2$], 14.1, 14.4 [2 $\times$ (2 C, $2 \times \text{ZnCH}_2\text{CH}_3$)], ca. 51–61 [very br., 12 C, $4 \times$ [2 C, $2 \times \text{N}_{\text{coord}}(\text{CH}_2\text{CH}_3)_2$]; 1 $\times$ [4 C, $2 \times \text{N}_{\text{uncoord}}(\text{CH}_2\text{CH}_3)_2$] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150.8 MHz, 213 K, $\text{C}_6\text{D}_5\text{CD}_3$): $\delta = 2.4$, 5.4 [2 $\times$ (2 C, $2 \times \text{ZnCH}_2\text{CH}_3$)], 12.3, 13.0 [2 $\times$ (2 C, $2 \times \text{ZnCH}_2\text{CH}_3$)], 13.6, 13.8, 13.9, 14.2, 14.7 [4 $\times$ [2 C, $2 \times \text{N}_{\text{coord}}(\text{CH}_2\text{CH}_3)_2$]; 1 $\times$ [4 C, $2 \times \text{N}_{\text{uncoord}}(\text{CH}_2\text{CH}_3)_2$]], 51.8, 53.8, 55.1, 56.4, 61.2 [4 $\times$ [2 C, $2 \times \text{N}_{\text{coord}}(\text{CH}_2\text{CH}_3)_2$]; 1 $\times$ [4 C, $2 \times \text{N}_{\text{uncoord}}(\text{CH}_2\text{CH}_3)_2$] ppm. $\text{C}_{32}\text{H}_{80}\text{N}_6\text{O}_6\text{Zn}_5$ (971.87): calcd. C 39.55, H 8.30, N 8.65; found C 38.93, H 8.07, N 8.41.

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- [14] Crystallographic details: Single-crystals of compounds **1–3** were mounted under inert perfluoro-polyether at the tip of a glass fibre and cooled in the cryostream of the diffractometer. The crystallographic data set of **1** was collected at 173(2) K with a Nonius Turbo CAD4 diffractometer; the data sets of **2** and **3** were measured at 198(2) K with a Nonius KappaCCD (both operated with graphite-monochromated Mo- K_α radiation; $\lambda = 0.71073$ Å). Data collection and reduction was performed with Express^[23a] and MolEN^[23b] (**1**), or with Collect^[23c] and Denzo-SMN^[23d] (**2** and **3**). The structures were solved by direct methods and refined against F^2 by full-matrix least-squares with SHELXS-97 (**1**)^[23e] and SHELXL-97 (**2** and **3**).^[23f] In the case of **2**, absorption correction was performed with SORTAV^[23g] CCDC-609256 (**1**), CCDC-609255 (**2**) and CCDC-617869 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. **1:** ($\text{C}_{16}\text{H}_{48}\text{N}_6\text{O}_6\text{Zn}_5$): $M_r = 747.47$, monoclinic, space group $C2/c$, $a = 12.910(1)$, $b = 11.851(2)$, $c = 20.324(2)$ Å, $\beta = 90.02(1)^\circ$, $V = 3109.2(7)$ Å³, $Z = 4$, $\rho_{\text{calcd.}} = 1.597$ g cm⁻³, $F(000) = 1536$, $\mu(\text{Mo-}K_\alpha) = 3.837$ mm⁻¹. A total of 4837 reflections were measured in the range $4.00^\circ \leq 2\theta \leq 53.88^\circ$, of which 3101 were unique ($R_{\text{int}} = 0.041$). Final R indices: $R_1 = 0.034$ [$I > 2\sigma(I)$], $wR_2 = 0.084$ (all data); max./min. residual electron density 0.89/–0.37 e Å⁻³. **2:** ($\text{C}_{24}\text{H}_{64}\text{N}_6\text{O}_6\text{Zn}_5 \cdot \text{C}_4\text{H}_{10}\text{O}$): $M_r = 933.78$, orthorhombic, space group $Pccn$, $a = 19.870(1)$, $b = 12.360(1)$, $c = 17.052(1)$ Å, $V = 4187.9(5)$ Å³, $Z = 4$, $\rho_{\text{calcd.}} = 1.481$ g cm⁻³, $F(000) = 1960$, $\mu(\text{Mo-}K_\alpha) = 2.867$ mm⁻¹. A total of 21700 reflections were measured in the range $3.88^\circ \leq 2\theta \leq 56.52^\circ$, of which 5139 were unique ($R_{\text{int}} = 0.028$). Final R indices: $R_1 = 0.031$ [$I > 2\sigma(I)$], $wR_2 = 0.074$ (all data); max./min. residual electron density 0.64/–0.54 e Å⁻³. **3:** ($\text{C}_{32}\text{H}_{80}\text{N}_6\text{O}_6\text{Zn}_5$): $M_r = 971.87$, monoclinic, space group Cc , $a = 16.480(1)$, $b = 11.595(1)$, $c = 25.073(1)$ Å, $\beta = 108.54(1)^\circ$, $V = 4542.4(5)$ Å³, $Z = 4$, $\rho_{\text{calcd.}} = 1.421$ g cm⁻³, $F(000) = 2048$, $\mu(\text{Mo-}K_\alpha) = 2.644$ mm⁻¹. A total of 9839 reflections were measured in the range $6.04^\circ \leq 2\theta \leq 55.88^\circ$, of which 9386 were unique ($R_{\text{int}} = 0.071$). Final R indices: $R_1 = 0.071$ [$I > 2\sigma(I)$], $wR_2 = 0.199$ (all data); max./min. residual electron density 1.83/–1.12 e Å⁻³.
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