

First mixed hydrazide/hydroxylamide metal aggregates†

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The first organometallic clusters of mixed hydrazide/hydroxylamide clusters of zinc, $[\text{Zn}(\text{MeZn})_4(\text{HNNMe}_2)_2(\text{ONEt}_2)_4]$ and $\{\text{Zn}(\text{EtZn})_4[\text{HNN}(\text{CH}_2)_5]_2(\text{ONEt}_2)_4\}$ were synthesized in one-pot synthesis protocols from dialkylzinc solutions, substituted hydrazines and *N,N*-diethylhydroxylamine; competing for the Zn atoms, the different binding properties of hydrazide and hydroxylamide ligands in these heteroleptic clusters are discussed.

Realising different stoichiometries of metal : non-metal atoms is a crucial requirement for the rational design of new molecular precursor compounds for many areas of material synthesis. The so far unknown zinc oxynitrides or nitrogen containing zinc oxide are promising but so far hardly accessible semiconductor materials.¹ Thus, a chemical synthesis route *via* thermolysis of molecular precursor compounds with suitable Zn : N : O stoichiometries would be highly desirable, but so far lack the accessibility of molecular precursor compounds. Recent contributions to this field are novel organometallic hydrazide and mixed hydrazide/alkoxide clusters of zinc having different core moieties such as Zn_4N_8 , $\text{Zn}_4\text{N}_6\text{O}$, $\text{Zn}_4\text{N}_4\text{O}_2$, $\text{Zn}_4\text{N}_2\text{O}_3$.^{2–4} The use of hydrazides for nitride material generation has been demonstrated earlier for Al and Ga,⁵ and the hydrazide chemistry of these elements has recently been reviewed.⁶

Besides hydrazides, hydroxylamide units are interesting components for the simultaneous introduction of N and O atoms into such metal compounds, and the weak N–N and N–O bonds provide predetermined breaking points for their thermal decomposition chemistry. In addition, both, hydrazide and hydroxylamide groups, introduce relatively low carbon contents. However, in contrast to the meanwhile well established hydroxylamide⁷ (and oximate⁸) compounds of Al and Ga, hydroxylamine compounds of zinc are almost unknown so far and the neutral hydroxylamine complex $(\text{H}_2\text{NOH})_2\text{ZnCl}_2$, Chrismer's salt,⁹ is the best known example.

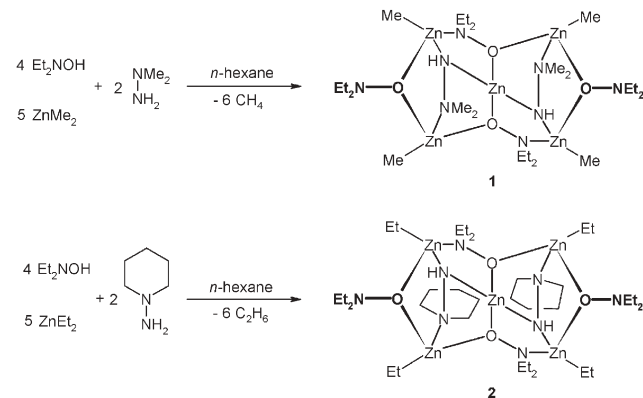
Combining the properties of hydrazine, N–N, and hydroxylamine units, N–O, in one metal compound is a concept which has so far not been realised and so we report here the first organometallic zinc compounds, containing both, hydrazide and hydroxylamide ligands.

As outlined in Scheme 1, dimethylzinc reacts cleanly with *N,N*-dimethylhydrazine and *N,N*-diethylhydroxylamine in a 2 : 1 : 1

ratio in *n*-hexane at ambient temperature to afford the pentazinc cluster **1**.[‡] Compound **1** was isolated as air-sensitive colourless plates (*ca.* 87% yield) and was characterised by ¹H and ¹³C NMR spectroscopy, by elemental analysis, mass spectrometry and single-crystal X-ray diffraction.[§] The ¹H NMR spectrum of **1** shows two signals for the methyl protons at zinc with equal intensity at –0.40 and –0.27 ppm. The chemical shifts of the protons of the ethylene groups at the hydroxylamine and the methyl groups at the hydrazine units appear almost in the same region. In the ¹H VT-NMR at 200 K, eight sets of ethylene protons of *N,N*-diethylhydroxylamine and two singlets for methyl protons on hydrazine units were observed. These data are fully consistent with molecular C₂ symmetry. The highest mass observed in the mass spectrum corresponds to the mass of the molecule diminished by that of one methyl group. A signal at 3184 cm^{–1} in the IR spectrum identified the NH functions.

Analogous to the synthesis of **1**, compound **2** was prepared by reacting Et₂Zn with 1-aminopiperidine and Et₂NOH in a 2 : 1 : 1 ratio in a one-pot-synthesis protocol (*ca.* 77% yield, Scheme 1).[‡] Compound **2** was characterised by NMR spectroscopy, elemental analysis and X-ray crystallography.[‡] The ¹H NMR signals of the hydroxylamine and hydrazine substituents and the ethyl groups at zinc overlap with one another and are thus difficult to assign even in a spectrum recorded at 200 K. The same scenario was also observed in the ¹³C NMR. The compound melts at 195 °C with decomposition. The IR signal at 3177 cm^{–1} confirms the presence of N–H bonds in the cluster.

In order to obtain higher hydrazide : hydroxylamide ratios, zinc alkyls, hydrazine and hydroxylamine were employed in different ratios from 2 : 1 : 1 to 2 : 2 : 1 to 2 : 3 : 1 under the same reaction conditions. However, the resulting products have the same composition and constitution as **1** and **2**, but lower yields were obtained.



Scheme 1

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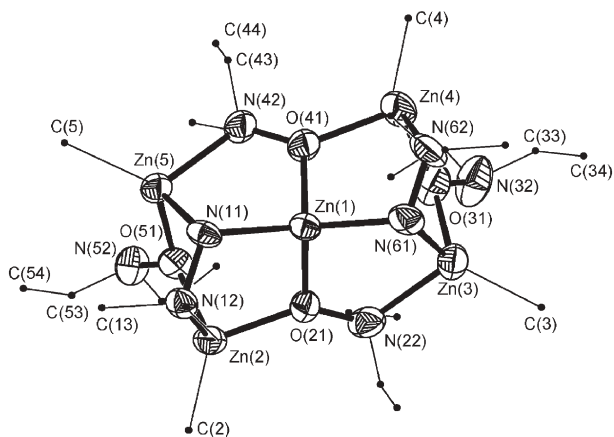


Fig. 1 Molecular structure of one of two crystallographically independent molecules of $[\text{Zn}(\text{MeZn})_4(\text{HNNMe}_2)_2(\text{ONeEt}_2)_4]$ **1** (50% probability ellipsoids). Carbon atoms are drawn as small circles and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Zn(1)–O(41) 1.961(4), Zn(1)–O(21) 1.965(4), Zn(1)–N(61) 1.979(4), Zn(1)–N(11) 1.987(4), Zn(2)–O(51) 1.989(4), Zn(2)–O(21) 2.023(4), Zn(2)–N(12) 2.192(4), Zn(2)–C(3) 1.990(6), Zn(3)–N(22) 2.201(5), Zn(5)–O(51) 2.023(4), Zn(5)–N(11) 2.093(4), Zn(5)–N(42) 2.178(5), N(11)–N(12) 1.450(6), N(22)–O(21) 1.423(6), N(32)–O(31) 1.460(6); O(41)–Zn(1)–O(21) 119.7(2), O(41)–Zn(1)–N(61) 95.0(2), O(21)–Zn(1)–N(61) 102.0(2), N(61)–Zn(1)–N(11) 145.2(2), C(2)–Zn(2)–O(51) 133.7(2), O(51)–Zn(2)–O(21) 95.9(2), O(51)–Zn(2)–N(12) 90.2(2), O(21)–Zn(2)–N(12) 86.4(2), O(31)–Zn(3)–N(22) 103.8(2), N(11)–N(12)–Zn(2) 105.4(3), N(22)–O(31)–Zn(2) 131.8(3), N(22)–O(21)–Zn(1) 116.2(3).

Single crystals of both compounds were grown from *n*-hexane solutions upon cooling and used for structure determination by X-ray diffraction. Compound **1** (Fig. 1) consists of a chalice shaped aggregate comprising six fused rings. Fig. 2 shows the molecular core of compound **1** and the C_2 axis passing through the atom Zn1 and bisecting the angle O(21)–Zn1–O(41). The central Zn atom, Zn(1), is connected to the anionic ends of two hydroxylamide and two hydrazide units. The “anionic” O and N binding sites of this formally dianionic $[\text{Zn}(\text{ONeEt}_2)_2(\text{NHNMe}_2)_2]^{2-}$ unit bind further four organometallic ZnMe units, while the neutral N atoms of these ONeEt₂ and NHNMe₂ substituents form rings by binding to these ZnMe moieties. As all zinc atoms of this formal $[\text{Zn}(\text{ONeEt}_2)_2(\text{NHNMe}_2)_2(\text{ZnMe})_4]^{2+}$ unit are only three-coordinate, their fourth coordination site is saturated by two further hydroxylamide units, each μ_2 -O-bridging two peripheral Zn atoms. This leaves one NEt₂ group non-coordinated.

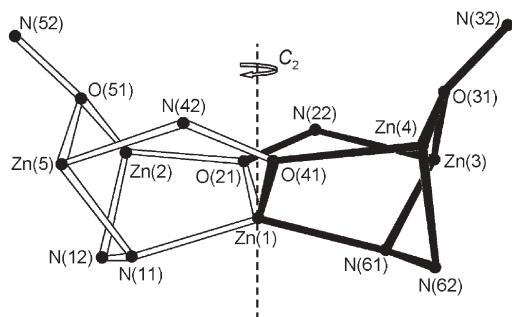


Fig. 2 $\text{Zn}_5\text{N}_8\text{O}_4$ core of compound **1**.

All six rings are five-membered, but have different constitution: two ZnONZnN rings include the central Zn atom and endocyclic NO units, two ZnNNZnO rings the central Zn atom and endocyclic NN units and the two peripheral ZnNNZnO rings also include an endocyclic NN unit.

This aggregation motif is entirely new and the closest relationship is that to a few pentanuclear species found *e.g.* in bioinorganics,¹⁰ but those contain square-planar coordinated central metal ions and contain no N–N bonds.

Zn–N bonds of different lengths are observed: the distance of Zn(1)–N(11) at 1.987(4) Å is shorter than the Zn(5)–N(11) bond to the peripheral Zn atom at 2.093(4) Å and is also about 0.1 Å shorter than Zn–N distance in tetrameric zinc hydrazide clusters.^{2,3} The same pattern is observed for the Zn–O bonds, where also those to the central Zn(1) are shortest at 1.961(4) Å, while there is a slightly longer Zn(5)–O(51) bond at 1.989(4) Å and two longer bonds, Zn(2)–O(21) and Zn(2)–O(51) at 2.023(4) Å.

The structure of **2** is shown in Fig. 3 and similar to that of **1**. The bulkiness of the substituents at the hydrazine unit and zinc do not alter the constitution and the aggregation motif.

An interesting feature of both compounds is that hydroxylamide rather than hydrazide units adopt the peripheral positions of the pentanuclear aggregate with one non-coordinate N atom. Obviously—and explainable through the more electron-withdrawing bonding partner oxygen—these hydroxylamides are weaker donors at these N atoms than the hydrazide ligands. In order to estimate the relative energies of the two isomeric forms, calculations on the relative energies (Table 1) of the isomers of

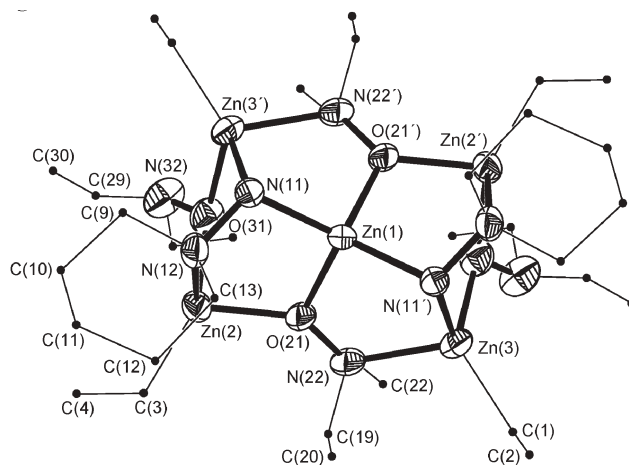
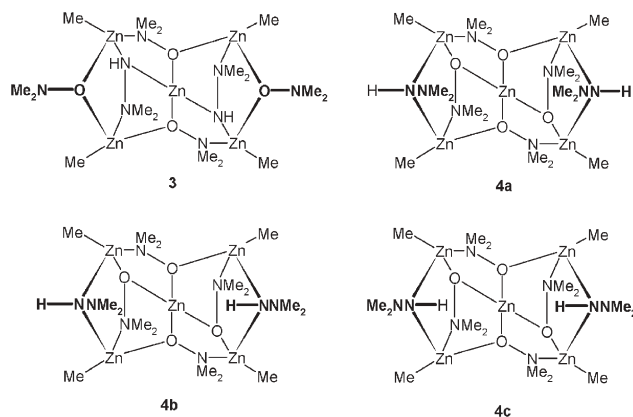


Fig. 3 Molecular structure of $\{\text{Zn}(\text{EtZn})_4[\text{HNN}(\text{CH}_2)_5]_2(\text{ONeEt}_2)_4\}$ **2** (50% probability ellipsoids). Carbon atoms are drawn as small circles and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Zn(1)–O(21) 1.956(5), Zn(1)–N(11) 1.986(6), Zn(2)–O(31) 2.008(6), Zn(2)–O(21) 2.047(6), Zn(2')–N(12) 2.273(4), Zn(2)–C(3) 1.984(12), Zn(3)–N(22) 2.228(8), Zn(3')–O(31') 2.022(6), Zn(3')–N(11) 2.080(6), N(11)–N(12) 1.468(8), N(22)–O(21) 1.445(8), N(32)–O(31) 1.465(9); O(21)–Zn(1)–O(21') 121.4(3), O(21)–Zn(1)–N(11) 96.0(2), O(21)–Zn(1)–N(11') 101.1(2), N(11)–Zn(1)–N(11') 144.6(4), C(3)–Zn(2)–O(31) 134.2(4), O(31)–Zn(2)–O(21) 93.3(2), O(31)–Zn(2)–N(12) 91.6(2), O(21)–Zn(2)–N(12) 85.1(2), O(31)–Zn(3')–N(22) 102.7(3), N(11)–N(12)–Zn(2) 102.4(4), N(22)–O(21)–Zn(2) 130.5(4), N(22)–O(21)–Zn(1) 116.3(5). Symmetry transformation to generate equivalent atoms marked with prime: $-x, y, \frac{1}{2} - z$.

Table 1 Relative energies of the isomers **3**, **4a**, **4b** and **4c** of $[\text{Zn}(\text{ZnMe})_4(\text{HNNMe}_2)_2(\text{ONMe}_2)_4]$ (Scheme 2) as calculated at the DFT(BP)/SV(P) level of theory

Isomer	3	4a	4b	4c
Relative energy/kJ mol ⁻¹	0	36	42	50



Scheme 2 Structures of the calculated isomers of the model compound $[\text{Zn}(\text{ZnMe})_4(\text{HNNMe}_2)_2(\text{ONMe}_2)_4]$ **3** and conformers of **4 (a–c)**.

the model compound $[\text{Zn}(\text{ZnMe})_4(\text{HNNMe}_2)_2(\text{ONMe}_2)_4]$ (Scheme 2) at the DFT(BP)/SV(P) level of theory were performed.

The core geometry of compound **1** corresponds well to the calculated values of the model **3** $[\text{Zn}(\text{ZnMe})_4(\text{HNNMe}_2)_2(\text{ONMe}_2)_4]$ with the same constitution, *i.e.* two ONMe_2 and two NHNMe_2 units bound to the central Zn atom (see ESI† for details). If four ONMe_2 units are bound to this central Zn atom, three possible conformers, **4a–c**, for the position of the hydrogen atoms and NMe_2 groups, respectively, have to be considered. They are all substantially higher in energy than the isomeric form **3**. The energy differences between the conformers **4a**, **4b** and **4c** are comparably small.

This comparison shows a clear preference of the mixed hydrazide/hydroxylamide aggregates to accept a hydrazide unit rather than a hydroxylamide unit for being incorporated into aggregate formation with all its three valences. The “homoleptic” zinc hydroxylamides also prefer aggregates of the type $[\text{Zn}(\text{ZnR})_4(\text{ONR}_2)_6]$ and are—in contrast to the above described heteroleptic hydroxylamide/hydrazide compounds—highly flexible in solution with the possibilities of adopting different aggregation modes and numbers.¹¹

We are now attempting to test the new chalice-like pentanuclear mixed hydrazide/hydroxylamides of zinc for their suitability as material precursors for N-doped zinc oxide.

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Notes and references

† *General procedure* for preparation of **1** and **2**: Under an inert atmosphere of dry nitrogen R_2Zn ($\text{R} = \text{Me}, \text{Et}$) (5.00 mL of a 2.0 M solution in toluene/*n*-hexane; 10.0 mmol) was added dropwise *via* syringe to a stirred solution of H_2NNMe_2 (0.40 mL, 5.22 mmol) or 1-aminopiperidine (0.54 mL, 5.00 mmol) and Et_2NOH (0.50 mL, 4.87 mmol) in *n*-hexane (20 mL) at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred for 6 h. The solvents were removed under reduced pressure; the resulting residue was dissolved in *n*-hexane and filtered. The clear, colourless filtrate was stored at –10 °C to afford colourless, plate like crystals. Spectroscopic data of compound **1** and **2** are available in the ESI.† Compound **1**: mp 164 °C (decomp.); compound **2**: mp 195 °C (decomp.). § *Crystal data*: **1**, $\text{C}_{24}\text{H}_{66}\text{N}_8\text{O}_4\text{Zn}_5$, $M = 857.70$, orthorhombic, space group *Pbca*, $a = 18.504(1)$, $b = 19.606(1)$, $c = 45.288(1)$ Å, $V = 16430.0(13)$ Å³, D_c ($Z = 16$) = 1.387 g cm⁻³, 55354 reflections collected on a Nonius Kappa CCD four-circle diffractometer [ω -scan, $2\theta_{\text{max}} = 50^\circ$, Mo-K α radiation, $\lambda = 0.71073$ Å, $T = 198(2)$ K] merged to 12713 unique ($R_{\text{int}} = 0.096$) refining to $R_1 = 0.055$ for 6894 data [$F_o > 4\sigma(F_o)$] and $wR_2 = 0.106$ for all 12713 data. **2**, $\text{C}_{24}\text{H}_{66}\text{N}_8\text{O}_4\text{Zn}_5$, $M = 993.93$, orthorhombic, space group *Pbcn*, $a = 11.369(2)$, $b = 15.909(3)$, $c = 25.860(5)$ Å, $V = 4677.3(15)$ Å³, D_c ($Z = 4$) = 1.411 g cm⁻³, 23657 reflections collected on an IPDS diffractometer [ω -scan, $2\theta_{\text{max}} = 49.2^\circ$, Mo-K α radiation, $\lambda = 0.71073$ Å, $T = 153(2)$ K] merged to 3498 unique ($R_{\text{int}} = 0.084$) refining to $R_1 = 0.076$ for 2902 data [$F_o > 4\sigma(F_o)$] and $wR_2 = 0.161$ for all 3498 data. All thermal displacement parameters for non-H-atoms were refined anisotropically (for **2** the atoms C1, C2, C3 and C4 were refined isotropically due to instabilities otherwise occurring in the refinement; this is due to the limited crystal quality), and for H-atoms isotropically.¹¹ For **1** only one of two structurally very similar independent molecules is discussed in this paper. Refinement using SHELXTL 6.10^{12a} and SHELXL-93.^{12b} CCDC 610379 and 610380. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608135e.

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