Synthesis and disruption of a tetrametallic zinc hydrazide

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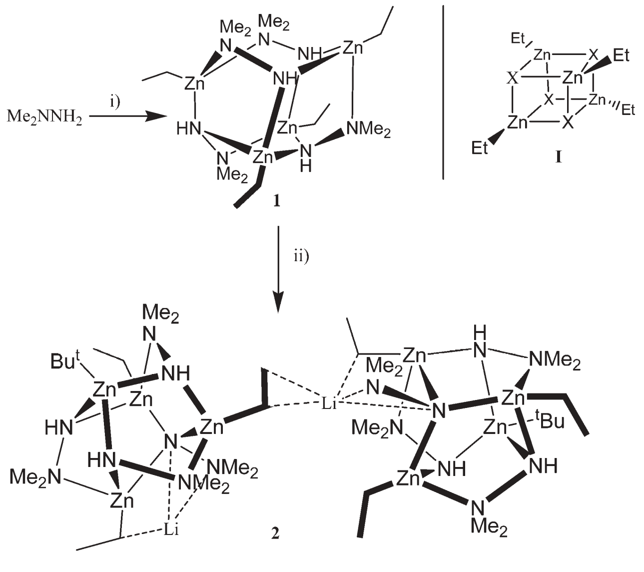
Treatment of 1,1′-dimethylhydrazine, Me_2NNH_2 with excess diethylzinc affords a novel tetrametallic Zn_4N_8 cage complex, which on further reaction with ^tBuLi forms a lithium-bridged chain of Zn_4N_7 cages.

In recent years, group 13 hydrazides have received attention principally for their potential as single source precursors to electronic materials, typically MN (M = Ga, Al).[1] These studies have spawned a number of unusual structural motifs, for example, we have found that 1,1′-dimethylhydrazine upon treatment with trimethylaluminium affords, following work-up, a novel octanuclear ring system – best viewed as a structural analogue of the calix[4]pyrrole.[2] Others have identified ladder-type structures,[3] and a Ga_4N_8 cage structure was isolated from the reaction of trimethylgallium with phenylhydrazine.[4] However, despite this research activity, there is a paucity of information regarding other main group element hydrazides.[5]

With this in mind, we have started to explore the chemistry of zinc alkyls in the presence of hydrazine ligands. Herein, we report our findings on the reaction of 1,1′-dimethylhydrazine with diethylzinc (Scheme 1), and find that the resulting novel tetrametallic zinc 'cube' can serve as a suitable starting material for further derivatization.



Scheme 1 *Reagents and conditions*: i) Et_2Zn, toluene, reflux, 3 h; ii) ^tBuLi, toluene, −78 °C, 6 h.

Reaction of Me_2NNH_2 with Et_2Zn (1.1 equivalents) in refluxing toluene affords, following work-up and recrystallization from acetonitrile, the colourless complex $[EtZn(NHNMe_2)]_4$ (**1**) in good yield (*ca.* 65%).† Complex **1** is doubtless formed *via* the loss of ethane, and can readily be prepared on a multigram scale. Unlike the analogous preparation involving trimethylaluminium, there is no insertion of nitrile here.[2] The ^1H NMR spectrum is rather complex, with numerous overlapping resonances for the ethyl, δ −0.14 to −0.32 (Zn–CH_2), 1.10 to 1.17 (Zn–CH_2CH_3) and dimethyl groups 2.36 and 2.72 ppm. In the IR spectrum, the ν(NH) peak is clearly observed at 3150 cm^{-1}. As expected, NMR studies indicate that **1** is not stable to prolonged exposure to air. Single crystals suitable for an X-ray diffraction study were obtained from a saturated acetonitrile solution on prolonged standing at ambient temperature. The solid-state structure (Fig. 1) reveals a novel tetrametallic cage structure in which tetrahedral zinc centres, each bearing one ethyl group, are linked *via* –$N(Me)_2NH$– bridging groups. Indeed, **1** can be viewed as a variation of the tetrameric structure **I** proposed for both ethylzinc chloride and bromide, where X = –$N(Me)_2NH$–.[6] There are two

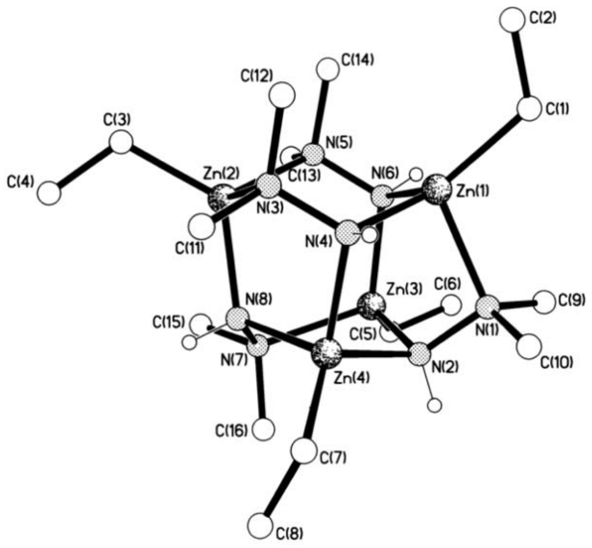


Fig. 1 Selected bond lengths (Å) and angles (°) for **1**: Zn(1)–N(1) 2.162(3), Zn(1)–N(4) 2.049(3), Zn(1)–N(6) 2.085(4), Zn(2)–N(3) 2.169(3), Zn(2)–N(5) 2.150(3), Zn(2)–N(8) 2.048(3), Zn(3)–N(2) 2.053(3), Zn(3)–N(6) 2.068(3), Zn(3)–N(7) 2.192(3), Zn(4)–N(2) 2.083(3), Zn(4)–N(4) 2.087(3), Zn(4)–N(8) 2.098(3); N(1)–Zn(1)–N(4) 93.96(12), N(4)–Zn(1)–N(6) 104.19(13), N(2)–Zn(3)–N(7) 93.23(11), N(2)–Zn(3)–N(6) 95.55(13), N(2)–Zn(4)–N(4) 97.77(12), N(2)–Zn(4)–N(8) 97.69(12).

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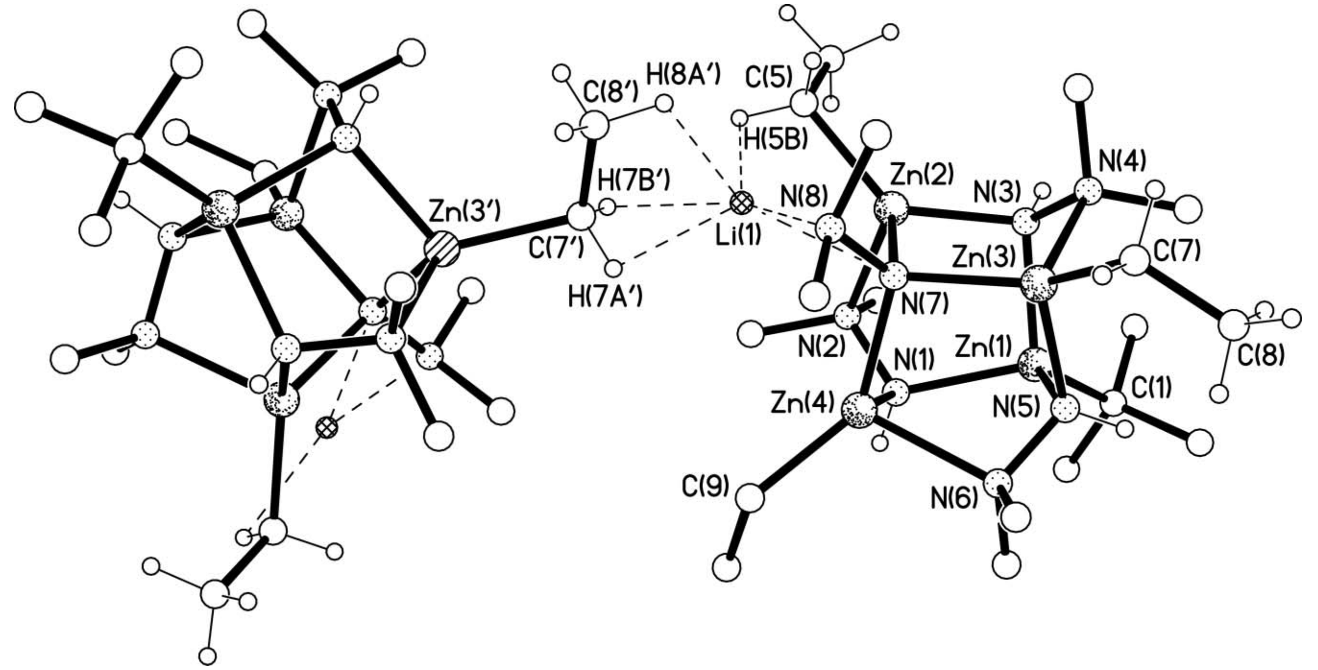

Fig. 2 Selected bond lengths (Å) and angles (°) for **2**: Zn(1)–N(1) 2.0751(13), Zn(1)–N(3) 2.1201(15), Zn(1)–N(5) 2.0809(13), Zn(2)–N(2) 2.1913(14), Zn(2)–N(3) 2.0197(14), Zn(2)–N(7) 2.0302(12), N(7)–N(8) 1.4918(17), Li(1)–N(7) 2.388(3), Li(1)–N(8) 1.934(3), Li(1)–H(5B) 2.19, Li(1)–C(5) 2.395, Li(1)–H(8A) 2.02, Li(1)–H(7A′) 2.06, Li(1)–H(7B′) 2.06, Li(1)–C(7′) 2.258(3), Li(1)–C(8′) 2.467(4); N(3)–Zn(1)–N(5) 97.80(5), N(1)–Zn(1)–C(1) 123.35(6), Zn(2)–N(7)–N(8) 113.57(9), N(6)–Zn(4)–N(7) 99.73(5).

6-membered rings: that containing Zn(1)/Zn(2) adopts a chair conformation, whilst the Zn(2)/Zn(3) ring is a twisted chair. These two 6-membered rings are linked *via* four 5-membered rings. Both Zn(1) and Zn(3) possess the same N_3C coordination environment, whereas Zn(2) and Zn(4) are different to one another, *viz.* NH + 2× NMe_2 + ethyl and 3× NH + ethyl, respectively. The Zn–NH bonds all fall in the range 2.048(3)–2.098(3) Å, whereas the Zn–NMe_2 bonds are somewhat longer [2.150(3)–2.192(3) Å] and are best considered dative. Although there are N–H groups present, the structure lacks any H-bonding, doubtless due to the paucity of acceptors. Overall, the structure adopts a layer motif, with the centroids of different molecules *ca.* 9 Å apart.

Given the presence of the NH functionality, it was of interest to establish the effect of deprotonation on the structural features of **1**. With this in mind, **1** was treated with ^{t}BuLi (1 equivalent) in toluene at −78 °C, which resulted in a colourless solution, from which small crystals suitable for X-ray diffraction using synchrotron radiation[7] could be isolated in moderate yield (*ca.* 25%).† The crystal structure (Figs. 2 and 3) reveals a remarkable chain-like structure in which the cages of **1** have been severely disrupted to afford new Zn_4N_7 cages that are linked *via* lithium bridges, *viz.* $[(ZnEt)_3(ZnBu^t)(NHNMe_2)_3(NNMe_2)(\mu\text{-Li})]_n$ **2**. Notable differences from the Zn_4N_8 cage of **1** include the now pendant $N(8)Me_2$ group at N(7), and the presence of a *tert*-butyl group at Zn(1), the source of which can only be the lithium reagent. Furthermore, the cages of **2** are made up solely of 5-membered ring systems. In the cages of **2**, three zinc centres (Zn(2)/(3) and (4)) possess the same N_3C coordination, each being bonded to NMe_2, NH, N(7) and an ethyl group, whereas Zn(1) is surrounded by three NH groups and the *tert*-butyl group. The pattern of Zn–N bond lengths is similar to **1**, *i.e.* Zn–N(H) 2.0197(4)–2.1201(15) Å and Zn–$N(Me)_2$ 2.1913(14)–2.2000(4) Å. For the lithium cation, there are a number of close 'agostic-type' contacts. The Li–H bonds to the neighbouring anion at H(7A′) [2.06 Å], H(7B′) [2.06 Å] and H(8A′) [2.02 Å] are similar to those found in the interstitial hydrides $\{Li_8(H)[N(2\text{-pyridyl})Ph]\}_6^{2+}$ [mean = 2.015 Å] and $\{Li_7(H)[N(2\text{-pyridyl})Ph]\}_6$ [2.06 Å],[8] whilst that to H(5B) [2.19 Å] is close to those observed in the interstitial hydride $[Li_8(H)(hpp)_6]^+$ [2.10–2.17 Å].[9] There is also a short Li–N(8) distance [1.934 Å], a somewhat longer bond to N(7) [2.388 Å], and long Li–C distances [2.258–2.467 Å]. Similar, long Li–C bonding [< 3.01 Å] has been implicated in a number of other systems.[10] The Li(1)–Zn distances are larger than the sum of their covalent radii [*ca.* 2.45 Å].

In summary, 1,1′-dimethylhydrazine reacts with diethylzinc to afford a novel tetrametallic Zn_4N_8 cage. Further reaction with ^{t}BuLi involves deprotonation, alkyl exchange and disruption of the zinc cage to afford a new Zn_4N_7 system; the latter link up *via* lithium bridges to afford a novel chain-like structure. Further

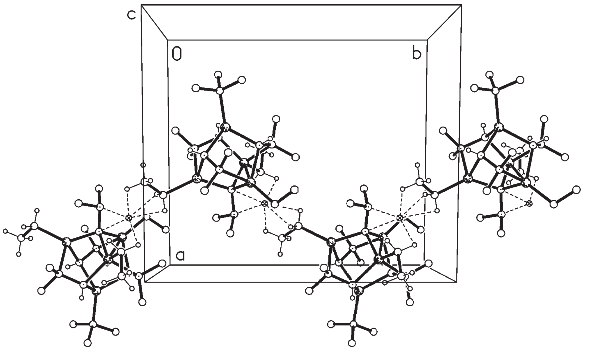

Fig. 3 Packing diagram of **2**.

investigations to survey the scope of this reaction, including the use of other hydrazines and deprotonating agents, are in progress.

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Notes and references

† Satisfactory microanalyses have been obtained for **1** and **2**. Selected spectroscopic data: For **1**: ^{1}H NMR ($CDCl_3$, 298 K, 400 MHz) δ: 2.77 (m, 12H, $N(CH_3)_2$), 2.36 (m, 12H, $N(CH_3)_2$), 2.31 (s 1H, N–*H*), 2.20 (s 1H, N–*H*), 2.08 (s 1H, N–*H*), 2.03 (s 1H, N–*H*), 1.14 (overlapping m, 12H, Zn–CH_2CH_3), −0.17 (q, 2H, $^2J_{HH}$ 8.2 Hz, Zn–CH_2), −0.22 (overlapping m, 4H, 2 × Zn–CH_2), −0.29 (q, 2H, $^2J_{HH}$ 8.1 Hz, Zn–CH_2). IR: ν(NH): 3149 cm^{-1}. Mass Spec (FAB$^+$): 585 ($M^+ - Et$). For **2**: ^{1}H NMR ($CDCl_3$, 298 K, 400 MHz) δ: 2.82–2.37 (overlapping m, 27H, 3x 'internal' $N(CH_3)_2$ + 'external' $N(CH_3)_2$ + 3N*H*), 1.25–0.91 (m, 9H, 3 × Zn–CH_2CH_3), 0.83 (s, 9H, + $(CH_3)_3$), 0.22 to −0.10 (m, 6H, Zn–CH_2CH_3). IR: ν(NH): 3172 cm^{-1}. Mass Spec (FAB$^+$): 553 ($M^+ - 3Et–Li$). *Crystal data* for **1**: $C_{16}H_{48}N_8Zn_4$, M = 614.10, monoclinic, space group $P2_1/n$, a = 11.5497(4), b = 14.6647(5), c = 16.2586(6) Å, β = 101.473(2)°, U = 2698.74(16) Å^3, T = 150(2) K, Z = 4, μ(Mo-Kα) = 3.529 mm^{-1}, λ = 0.71073 Å, 20882 reflections measured, 5280 unique (R_{int} = 0.019) which were used in all calculations. The final $wR2$ = 0.106 (all data) and $R1$ = 0.037 (for 4641 data with $F^2 > 2\sigma(F^2)$). *Crystal data* for **2**: $C_{18}H_{51}LiN_8Zn_4$, M = 648.09, monoclinic, space group $P2_1/c$, a = 12.9610(6), b = 14.6764(7), c = 15.5138(7) Å, β = 98.069(2)°, U = 2921.8(2) Å^3, T = 151(2) K, Z = 4, μ = 3.263 mm^{-1}, synchrotron radiation at Daresbury Laboratory, Station 9.8, silicon 111 monochromator, λ = 0.6765 Å, 34776 reflections measured, 9877 unique (R_{int} = 0.032) which were used in all calculations. The final $wR2$ = 0.079 (all data) and $R1$ = 0.029 (for 8625 data with $F^2 > 2\sigma(F^2)$). CCDC 290422 & 290423. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516431a

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