Terminal Zinc–Hydrogen Bonding. *X*-Ray and Neutron Diffraction Studies of 2-Dimethylaminoethyl(methyl)aminozinc Hydride Dimer

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Summary The crystal structure of the title compound reveals that hydrogen bound to zinc occupies a terminal position and that each zinc atom is four co-ordinate by virtue of the formation of four- and five-membered rings with the diamine.

RECENTLY zinc hydride complexes of the type $(RZnH.Py)_3$ (R = Et, Ph)[1] (Py = pyridine) and $(C_5H_6N)Zn_3H_5.Py_2$,[2] in which hydrogen is believed to play a bridging role between two metal atoms, have been prepared. Although hydrogen in beryllium hydrides normally occupies a bridging position,[3] no diffraction data were available to establish the role of hydrogen in zinc hydrides prior to the investigations reported here.

Crystal data: needles of $[HZnN(Me)C_2H_4NMe_2]_2$, crystallised from toluene solution,[4] are monoclinic, space group $P2_1/c$, $a = 6{\cdot}372(3)$, $b = 11{\cdot}317(5)$, $c = 11{\cdot}977(5)$ Å, $\beta = 111{\cdot}75(8)°$, $Z = 2$ molecules of dimer, $D_c = 1{\cdot}39$, $D_m = 1{\cdot}39$–$1{\cdot}41$ g cm^{-3}. The structure was solved by Patterson and Fourier methods from photographic *X*-ray data (Cu-K_α radiation) collected by the equi-inclination Weissenberg technique for the layers hkl ($h = 0$–4). For the 1000 observed *X*-ray reflexions, R converged to 0·109. Low temperature (−150 °C) neutron diffraction using Normal Beam Weissenberg geometry at the U.K.A.E.R.E. Harwell yielded 337 independent reflexions for which $I_{obs} \geqslant 4\sigma(I_{obs})$. All 14 hydrogen atoms showed up clearly from a difference Fourier map using neutron structure factors calculated using the Zn, N, and C positions found from the *X*-ray determination.

The atomic parameters of all 22 atoms were refined from the neutron diffraction data using least-squares methods with isotropic temperature factors throughout. The refinement converged to an R-value of 0·114 after 11 cycles with the block-diagonal approximation and finally 3 cycles of full matrix treatment. With the exception of the Zn–H distance which is based on the neutron diffraction data, all the angles and distances reported here are those derived from the *X*-ray data.‡

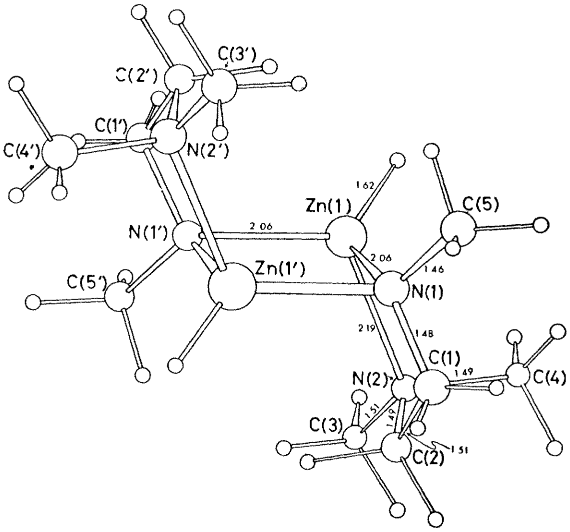

FIGURE Structure of $[HZnN(Me)C_2H_4NMe_2]_2$. Hydrogen atoms are unlabelled.

The complex is dimeric in the solid state as well as in benzene solution.[4] The zinc atoms achieve four-co-ordination by participating in two co-ordinate bonds, each with nitrogen, one, involving N(1), resulting in a four-membered ring about the centre of symmetry and the other, involving N(2), giving rise to two five-membered rings. The atoms N(1), C(1), and C(5) all lie almost in a plane at right

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

angles to the plane of the Zn_2N_2 ring. The zinc–nitrogen bond lengths in the four-membered ring are both 2·06 Å and are not significantly different from the bond lengths (mean 2·07 Å) found in the Zn_2N_2 ring in $(MeZnNPh_2)_2$[5] but are shorter than the zinc–nitrogen bond lengths in the five-membered ring (2·19 Å). The N(1)–Zn–N(1′) angle (92°) in the ring is greater than the Zn–N(1)–Zn′ angle but distortions of bond angles at zinc are to be expected as a consequence of the presence of a particularly small atom (hydrogen) in one co-ordination position and the simultaneous participation of the atoms Zn and N(1) in both a four-membered and a five-membered ring. The two angles Zn–N(1)–C(5) and Zn′–N(1)–C(5) (119 and 117°), are considerably greater than the tetrahedral value, no doubt as a result of the Zn–N(1)–Zn′ angle being constrained to 88°. The other three angles at N(1) do not differ significantly from the tetrahedral value.

A greater distortion is found at N(2): C(3)–N(2)–Zn (120°) and C(2)–N(2)–C(4) (113°) are greater while C(2)–N(2)–Zn (102°) and C(4)–N(2)–Zn (103°) are smaller than the tetrahedral value. The distortions are understandable in terms of the alleviation of the shortest non-bonding carbon–carbon contact (2·98 Å) namely that between C(4) and C(1). The zinc–zinc separation (2·86 Å) is greater than the sum (2·62 Å) of the Pauling tetrahedral covalent radii. There is no significant interaction between dimeric units and there can be no question of hydrogen bridging between zinc atoms of different dimeric units as the shortest contact between zinc atoms not of the same dimer is greater than 5 Å. The terminal Zn–H bond length (1·62 Å) agrees with the sum of the constituent covalent radii (1·62 Å).

The complex shows a broad i.r. absorption at 1695 cm^{-1} (Nujol mull) erroneously reported earlier as 1825 cm^{-1} which can be ascribed to a Zn–H vibration and this is in a similar region to that found (1640 cm^{-1}) for $PhZn_2H_3$.[6]

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