intermolecular $H \cdots H$ contacts $\leq 2 \cdot 8$ Å per molecule. This number is 30 in the ruthenocene structure compared with 23–25 in triclinic ferrocene and 22 in monoclinic nickelocene. Note that H(4), on the mirror plane, makes no intermolecular contact $< 2 \cdot 8$ Å (there are some just $> 2 \cdot 8$ Å).

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Terminal Zinc–Hydrogen Bonding. X-ray and Neutron Diffraction Studies of the (2-Dimethylamino-*N*-methylethylamido)hydridozinc Dimer*

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Abstract

$C_{10}H_{28}N_4Zn_2$, $M_r = 670 \cdot 2$, monoclinic, $P2_1/c$, at 293 K $a = 6 \cdot 372$ (3), $b = 11 \cdot 317$ (5), $c = 11 \cdot 977$ (5) Å, $\beta = 111 \cdot 75$ (8)°, $U = 802 \cdot 1$ Å^3, $Z = 2$ dimer units, $D_m = 1 \cdot 40$ (1), $D_c = 1 \cdot 39$ Mg m^{-3}, μ(Cu $K\alpha$) = 3·67 mm^{-1}, $F(000) = 352$. The structure was determined from photographic X-ray data. For the 1000 reflections classified as observed R converged to 0·109. Low-temperature (123 K) neutron diffraction yielded 337 independent reflections. All 14 H atoms showed up on a difference map obtained with neutron structure factors calculated from the Zn, N and C positions

found from the X-ray determination. The compound is dimeric in the solid as well as in benzene solution. A four-membered Zn_2N_2 ring links the two halves of the dimer round a centre of symmetry and a second, albeit weaker, dative bond involving the second N atom results in the formation of five-membered rings and brings the coordination number of the Zn atom to four. The H atom bonded to Zn occupies a terminal position.

Introduction

The preparation of $RMN(Me)C_2H_4NMe_2$ (R = alkyl) has been reported for M = Be (Coates & Roberts, 1968), Mg (Coates & Heslop, 1968) and Zn (Coates & Ridley, 1965). Such compounds are dimeric in benzene solution and structures have been suggested for them, but up to the time when the present work began no crystal structure data were available concerning either these compounds or the related species $HMN(Me)C_2H_4NMe_2$ which has been reported for M = Be and Zn (Bell & Coates, 1968). Furthermore no

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crystalline compound containing a Zn—H bond had previously been available for examination by diffraction methods and, in view of the fact that H bonded to Be generally occupies a bridging rather than a terminal position (Coates & Morgan, 1970), we decided to examine the crystal structure of the title compound.

Recently, other zinc hydride complexes of the type $(RZnHpy)_3(R = Et, Ph)$ (De Koning, Boersma & Van der Kerk, 1978) and $(C_5H_6N)Zn_3H_5py_2$ (De Koning, Boersma & Van der Kerk, 1977), in which H is believed to play a bridging role between two metal atoms, have been prepared.

A preliminary report of the crystal structure detailed herein has been published (Bell, Moseley, Shearer & Spencer, 1980).

Experimental

(2-Dimethylamino-N-methylethylamido)hydridozinc was prepared as previously described from zinc hydride and N,N,N'-trimethylethylenediamine (Bell & Coates, 1968). Recrystallization of the colourless crystals from toluene yielded needles which were sealed in Pyrex capillaries under dry nitrogen. The needle used for X-ray data collection was $0.24 \times 0.52 \times 1.5$ mm, elongated along **a**. The crystals used for the neutron data collection were grown from toluene solution as parallelepipeds developed along [011] and were sealed in silica tubes.

The density was determined by flotation in mixtures of trifluorobenzene and perfluorobutylamine.

X-ray data were recorded by the equi-inclination Weissenberg technique with Ni-filtered Cu $K\alpha$ radiation for nkl type nets $n = 0-4$. For high-order reflections which were split owing to the resolution of the $K\alpha_1, K\alpha_2$ doublet the intensity of the reflection due to the $K\alpha_1$ component alone was measured and was multiplied by an empirical correcting factor of 1.32. Corrections were made for Lorentz and polarization factors and for spot-extension effects for upper levels.

Integrated neutron intensities were measured at 123 K with a Hilger & Watts diffractometer attached to the DIDO reactor at AERE, Harwell. Two sets of data obtained in separate diffractometer runs (run 1 $\lambda = 1.104$ Å, run 2 $\lambda = 1.009$ Å) were placed on the same relative scale through common reflections. The two crystals used were very small (4.6 and 3.8 mm³ respectively) and no corrections for extinction or absorption were applied. The intensities of the 337 independent reflections for which $I_o \geq 4\sigma I_o$ were corrected for the Lorentz factor.

Structure solution and refinement

The structure was solved by Patterson and Fourier methods from the X-ray data. Least-squares refine-

Table 1. *Fractional positional parameters* ($\times 10^4$, $\times 10^5$ *for* Zn) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses (from the X-ray data)*

The B_{eq} values were calculated by reference to Willis & Pryor (1975).

	x	y	z	B_{eq} (Å²)
Zn	9568 (30)	10123 (13)	−3511 (12)	3·97 (10)
N(1)	1452 (19)	215 (8)	1274 (8)	4·0 (3)
N(2)	−556 (21)	2428 (9)	342 (9)	4·5 (4)
C(1)	602 (30)	990 (11)	2008 (9)	4·7 (5)
C(2)	−1269 (33)	1792 (12)	1229 (13)	5·3 (6)
C(3)	−2528 (34)	3116 (14)	−509 (15)	6·1 (7)
C(4)	1392 (31)	3233 (15)	925 (17)	5·8 (7)
C(5)	3687 (30)	−231 (14)	1995 (13)	5·7 (6)

Table 2. *Fractional positional parameters* ($\times 10^4$) *and isotropic thermal parameters* (Å²) *with e.s.d.'s in parentheses (from the neutron data)*

$$T = \exp(-B_{iso} \sin^2 \theta / \lambda^2).$$

	x	y	z	B_{iso}
Zn	986 (32)	1001 (20)	−398 (22)	0·7 (4)
N(1)	1446 (17)	191 (12)	1329 (12)	0·0 (3)
N(2)	−541 (22)	2430 (13)	358 (14)	0·5 (3)
C(1)	578 (43)	975 (25)	2020 (26)	2·5 (5)
C(2)	−1288 (28)	1809 (20)	1293 (18)	0·5 (4)
C(3)	−2470 (32)	3107 (23)	−468 (21)	1·1 (4)
C(4)	1409 (31)	3173 (22)	953 (21)	0·9 (4)
C(5)	3715 (38)	−219 (25)	2060 (23)	2·1 (5)
H(1)	2012 (54)	1488 (33)	2649 (36)	1·0 (7)
H(2)	−26 (87)	458 (56)	2651 (52)	4·2 (1·1)
H(3)	−1807 (58)	2470 (47)	1808 (41)	2·1 (8)
H(4)	−2886 (67)	1322 (41)	728 (43)	1·9 (8)
H(5)	−3746 (67)	2502 (44)	−894 (40)	2·3 (9)
H(6)	−1973 (54)	3474 (36)	−1170 (34)	1·2 (7)
H(7)	−2937 (72)	3815 (47)	−6 (47)	2·9 (9)
H(8)	2933 (97)	2689 (63)	1530 (60)	5·1 (1·4)
H(9)	1743 (78)	3587 (53)	248 (51)	3·5 (1·0)
H(10)	955 (72)	3781 (46)	1493 (46)	2·5 (9)
H(11)	3606 (82)	−827 (61)	2730 (53)	4·3 (1·1)
H(12)	5053 (70)	413 (42)	2505 (42)	2·6 (9)
H(13)	4519 (73)	−759 (50)	1527 (46)	3·2 (8)
H(14)	2790 (79)	1572 (51)	−927 (50)	3·7 (1·0)

ment of positional and thermal parameters for the Zn, N and C atoms converged to $R = 0.109$. The final values of the atomic parameters from the X-ray study are given in Table 1.

All 14 H atoms showed up in a difference map obtained with neutron structure factors calculated from the Zn, N and C atom positions derived from the X-ray study.

The parameters of all 22 atoms were refined by least squares with the neutron diffraction data and with isotropic temperature factors and unit weights throughout. The neutron scattering lengths were 5·9, 9·4, 6·6 and −3·74 fm for Zn, N, C and H respectively. The refinement converged to $R = 0.114$ when the 66

positional parameters, 22 thermal parameters and the overall scale factor were treated as a single 89-square matrix.

Final atomic parameters from the neutron refinement are given in Table 2.*

Description and discussion of structure

The molecular arrangement of the $[HZnN(Me)C_2H_4NMe_2]_2$ dimer is shown in Fig. 1. The Zn atoms are four-coordinate and participate in two coordinate bonds each with N, the 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.

N(1), C(1) and C(5) all lie within 0·01 Å of a plane through the origin which is almost at right angles (88·9°) to the plane of the Zn_2N_2 ring. Details of these planes are given in Table 3.

A comparison of the bond lengths and angles obtained from the X-ray and neutron diffraction studies is given in Tables 4 and 5. The bond lengths and angles quoted in the text are those obtained from the X-ray data except where stated otherwise.

The Zn–N lengths in the four-membered ring (2·060 and 2·062 Å) are not significantly different from the lengths (mean 2·07 Å) found in the Zn_2N_2 ring in $(MeZnNPh_2)_2$ (Spencer, 1967) but are shorter than that in the five-membered ring (2·186 Å). Evidently participation in the four-membered ring renders the bond between Zn and N(1) stronger than that between Zn and N(2). This may be due in part to synergic bonding in the small ring but steric effects, to be described later,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35639 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
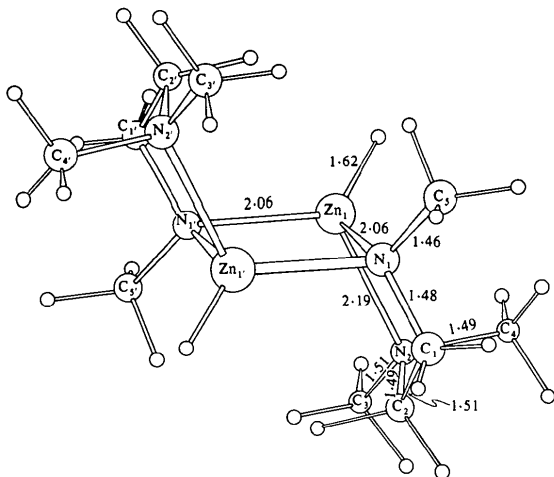

Fig. 1. Structure of $[HZnN(Me)C_2H_4NMe_2]_2$.

Table 3. Equations of least-squares planes referred to orthogonal axes with distances (Å) of relevant atoms from the planes in square brackets

Symmetry code: none, x,y,z; ('), $-x,-y,-z$.

Plane (A): N(1), C(1), C(5), N(1'), C(1'), C(5')

$$0.4111X + 0.7893Y - 0.4561Z = 0.0000$$

[N(1), 0·006 (11); C(1), −0·002 (15); C(5), −0·002 (17)]

Plane (B): Zn(1), Zn(1'), N(1), N(1')

$$0.7124X - 0.5773Y - 0.3990Z = 0.0000$$

Table 4. Comparison of bond lengths (Å) derived from (a) the neutron data, and (b) the X-ray data

	(a) Neutron data (123 K) $a = 6·284, b = 11·298,$ $c = 11·796$ Å, $\beta = 111·75°$	(b) X-ray data (293 K) $a = 6·372, b = 11·317,$ $c = 11·977$ Å, $\beta = 111·75°$
Zn–H(14)	1·618 (61)	
Zn–N(1)	2·152 (26)	2·060 (10)
Zn–N(1')	2·028 (26)	2·062 (11)
Zn–N(2)	2·227 (27)	2·186 (11)
N(1)–C(1)	1·441 (31)	1·480 (16)
N(1)–C(5)	1·442 (30)	1·455 (21)
N(2)–C(2)	1·521 (26)	1·488 (18)
N(2)–C(3)	1·459 (28)	1·507 (22)
N(2)–C(4)	1·435 (27)	1·488 (22)
C(1)–C(2)	1·501 (35)	1·514 (23)
C(1)–H(1)	1·10 (5)	
C(1)–H(2)	1·12 (7)	
C(2)–H(3)	1·09 (5)	
C(2)–H(4)	1·12 (5)	
C(3)–H(5)	1·03 (5)	
C(3)–H(6)	1·07 (5)	
C(3)–H(7)	1·07 (6)	
C(4)–H(8)	1·09 (7)	
C(4)–H(9)	1·04 (6)	
C(4)–H(10)	1·05 (6)	
C(5)–H(11)	1·07 (7)	
C(5)–H(12)	1·08 (5)	
C(5)–H(13)	1·12 (6)	

will also contribute to the difference between the two types of Zn–N length.

The sum of the Pauling covalent radii for Zn and N is 2·01 Å and the observed Zn–N distances are consistent with a degree of polar character in the Zn–N bond.

The N–C lengths are all the same within the limits of experimental error, mean 1·48 Å. This compares well with those in ethylamine (1·47 Å) (Allen & Sutton, 1950) and in the tetramethylethylenediamine (TMED) moiety in AlH_3TMED (mean 1·48 Å) (Palenik, 1964).

The C–C length (1·51 Å) also appears to be normal since it is not significantly different from the value (1·54 Å) found in diamond.

Table 5. *Comparison of bond angles (°) with e.s.d.'s in parentheses from (a) the neutron data and (b) the X-ray data*

	(a)	(b)
N(1)–Zn(1)–N(1')	92·3 (10)	92·0 (4)
N(1)–Zn(1)–N(2)	81·7 (9)	84·1 (4)
N(1')–Zn(1)–N(2)	110·4 (11)	110·6 (5)
N(1)–Zn(1)–H(14)	131·9 (24)	
N(1')–Zn(1)–H(14)	123·5 (24)	
N(2)–Zn(1)–H(14)	109·4 (23)	
Zn(1)–N(1)–Zn(1')	87·7 (10)	88·0 (4)
Zn(1)–N(1)–C(5)	117·3 (14)	119·1 (9)
Zn(1)–N(1)–C(1)	109·2 (15)	109·9 (7)
Zn(1')–N(1)–C(5)	119·3 (14)	117·1 (9)
Zn(1')–N(1)–C(1)	110·3 (14)	110·7 (9)
C(1)–N(1)–C(5)	110·9 (18)	110·2 (11)
C(2)–N(2)–C(4)	110·6 (15)	112·5 (12)
C(2)–N(2)–C(3)	108·8 (15)	109·6 (13)
C(3)–N(2)–C(4)	111·6 (16)	109·9 (12)
C(2)–N(2)–Zn(1)	104·5 (12)	102·2 (8)
C(3)–N(2)–Zn(1)	119·2 (14)	119·8 (9)
C(4)–N(2)–Zn(1)	101·7 (13)	102·6 (10)
N(1)–C(1)–C(2)	116·2 (21)	111·5 (10)
N(2)–C(2)–C(1)	108·6 (18)	110·6 (14)
H(1)–C(1)–C(2)	102·9 (44)	
H(3)–C(2)–C(4)	106·3 (38)	
H(5)–C(3)–H(6)	106·0 (39)	
H(6)–C(3)–H(7)	108·6 (40)	
H(7)–C(3)–H(5)	115·7 (44)	
H(8)–C(4)–H(9)	109·5 (52)	
H(9)–C(4)–H(10)	111·9 (47)	
H(10)–C(4)–H(8)	108·8 (49)	
H(11)–C(5)–H(12)	108·5 (48)	
H(12)–C(5)–H(13)	101·6 (43)	
H(13)–C(5)–H(11)	103·3 (48)	

Table 6. *Intra- and intermolecular non-bonding contacts <4 Å*

Equivalent positions

(1)	x, y, z		(3)	$-x$, $-y$, $-z$
(2)	$-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$		(4)	x, $\frac{1}{2}-y$, $\frac{1}{2}+z$

A	B	Equivalent position	$A\cdots B$ (Å)
Zn	Zn	3	2·864 (3)
Zn	C(4)	1	2·901 (19)
Zn	C(1)	3	2·932 (14)
Zn	C(5)	3	3·016 (17)
Zn	C(5)	1	3·046 (17)
Zn	C(3)	1	3·213 (19)
Zn	C(2)	3	3·372 (17)
Zn	N(2)	3	3·902 (12)
N(1)	N(2)	1	2·845 (16)
N(1)	N(1)	3	2·964 (15)
C(1)	C(4)	1	2·978 (24)
C(3)	C(5)	3	3·662 (25)

A	B	Equivalent position	Cell	$A\cdots B$ (Å)
C(3)	C(5)	4	(−1,1,0)	3·891 (25)
C(4)	C(5)	2	(1,0,0)	3·643 (26)

Unless otherwise stated the equivalent position refers to the cell (0,0,0).

Fig. 2. [HZnN(Me)C$_2$H$_4$NMe$_2$]$_2$ – projection on the (010) plane.

Both kinds of atoms involved in the central ring are four-coordinate and in terms of covalent bonding would formally be considered to be sp^3-hybridized. The N(1)–Zn–N(1') angle in the ring is greater than the Zn(1)–N(1)–Zn(1') angle (88·0°) but it is not easy to draw conclusions from this as distortion of the bond angles at Zn are to be expected as a consequence of the presence of the small H atom in one coordination position. The picture is further complicated by the simultaneous participation of Zn and N(1) in both a four- and a five-membered ring.
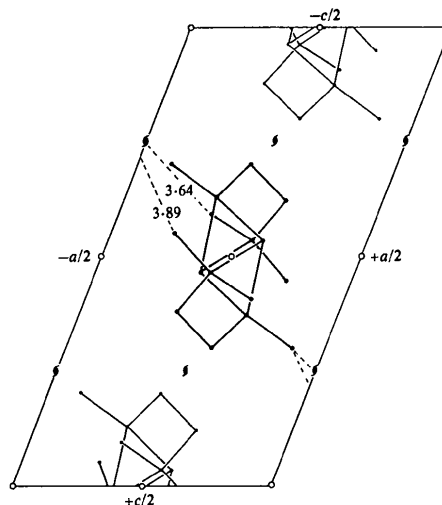
The two angles Zn(1)–N(1)–C(5) and Zn(1')–N(1)–C(5) (119·1 and 117·1°) are considerably greater than the tetrahedral value, which is no doubt a result of the Zn–N(1)–Zn(1') angle being constrained to 88·0°. The other three angles at N(1) do not differ significantly from the tetrahedral value.

A greater range of bond angles is found at N(2); C(3)–N(2)–Zn(1) (119·8°) and C(2)–N(2)–C(4) (112·5°) are greater, while C(2)–N(2)–Zn(1) (102·2°) and C(4)–N(2)–Zn(1) (102·6°) are smaller than the tetrahedral value. These distortions are understandable in terms of a movement to alleviate the

shortest non-bonding C$\cdots$C contact (2·98 Å) between C(4) and C(1).

Steric interferences involving C(3) and/or C(4) must tend to contribute to the lengthening of the Zn(1)–N(2) bond. The intramolecular and intermolecular non-bonding contacts <4 Å are given in Table 6. Contacts between C atoms bonded to a common atom are not included.

The Zn$\cdots$Zn separation (2·86 Å) is greater than the sum (2·62 Å) of the Pauling tetrahedral covalent

radii. The shortest contact that the Zn makes with a methyl C atom (2·90 Å) involves C(4) and this situation would be made worse by a shortening of the Zn(1)—N(2) bond.

The short N···N contacts (2·85 and 2·96 Å) are those across the four- and five-membered rings respectively. Both are much greater than the sum (1·40 Å) of the tetrahedral covalent radii of two N atoms.

The intermolecular packing is shown in Fig. 2 which is a projection along **b**. Only two of the approach distances are <4·0 Å and both of these are >3·6 Å so that there does not appear to be any significant interaction between separate dimer molecules. The C—H bond lengths all appear to be normal compared with previously published lengths (Sequeira, Rajagopal & Chidambaram, 1972) and with the sum of the covalent radii for C and H (1·09 Å).

The zinc–hydrogen bond

The neutron diffraction study has provided a reliable position for the H atom attached to Zn with a bond length of 1·618 Å, not significantly different from the value (1·59 Å) obtained for a short-lived species by spectroscopic methods (Herzberg, 1950). The length of the Zn—H bond is close to the sum (1·62 Å) of the covalent radii (Sanderson, 1976) and much less than the sum of the ionic radii, 2·82 Å (Pauling, 1960), suggesting that the bond is predominantly covalent in character.

In contrast to the beryllium hydrides where Be···H···Be bridging predominates, there can be no question of H bridging between Zn atoms in the present compound since the shortest contact between Zn atoms not of the same dimer is >5 Å.

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The Structure of Tris(1-pyrrolidinecarbodithioato)antimony(III)

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Abstract

The crystal structure of $[Sb(C_5H_8NS_2)_3]$ has been determined from three-dimensional intensities, measured on a computer-controlled Philips PW 1100 single-crystal diffractometer (1904 observed reflexions). The cell constants, obtained from direct θ-value measurements on the diffractometer, are: $a = 16·442$ (1), $b = 11·883$ (1), $c = 23·677$ (2) Å, $\beta = 102·95$ (1)°, $Z = 8$; the space group is $C2/c$. The