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Dimeric Methyl(diphenylamino)zinc,* C₂₆H₂₆N₂Zn₂

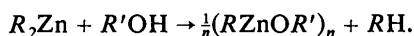
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Abstract. $M_r = 497.27$, orthorhombic, $P2_12_12_1$, $a = 7.57$ (2), $b = 14.95$ (3), $c = 20.43$ (4) Å, $U = 2312.09$ Å³, $Z = 4$, $D_m = 1.43$ (2), $D_x = 1.43$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 2.7$ mm⁻¹, $F(000) = 1024$, $T = 295$ K, $R = 0.086$ for 2110 observed reflections. The molecule is dimeric in the solid state as in solution, with the MeZn units bridged by two NPh₂ units to give a Zn₂N₂ ring in which all the angles are close to 90° so that the zinc atoms are three-coordinate and the nitrogen atoms are four-coordinate.

Introduction. Reactions between R₂Zn and bases containing acidic hydrogen atoms in 1:1 molar proportions result in the elimination of hydrocarbon, e.g.



The product, if monomeric, would contain a coordinatively unsaturated metal atom attached to a donor atom, which because of the dipole $M^{\delta+}$ -ligand $^{\delta-}$ would have increased donor properties with the resulting formation of either internal coordination or associated compounds. Because of size and energy constraints, internal coordination has not been observed in Zn compounds and appears to be limited to first-row elements. Degrees of association of two, three, four, five, six and eight have been found for organozinc complexes, formed as above, containing N (Coates & Ridley, 1965; Noltes & Boersma, 1967; Pattison & Wade, 1968), O (Coates & Ridley, 1965, 1966;

Schindler, Schmidbaur & Krüger, 1965; Shearer & Spencer, 1980), S (Coates & Ridley, 1965; Adamson & Shearer 1969; Adamson, Bell & Shearer, 1982) and halogen (Boersma & Noltes, 1966; Moseley & Shearer, 1963). Several factors have been considered to influence the degree of association. With alcohols and thiols, the donor atom makes use of both lone pairs of electrons so that many organozinc alkoxides are tetrameric like (MeZnOMe)₄ (Shearer & Spencer, 1980) except where bulky organic groups present make the formation of smaller oligomers more favourable (Coates & Ridley, 1965). In contrast, sulphides show larger degrees of association, so that MeZnSP r^i is hexameric in benzene solution (Coates & Ridley, 1965), though octameric in the solid state (Adamson & Shearer, 1969), whereas MeZnSBU t , and EtZnSBU t are pentameric in benzene (Coates & Ridley, 1965), the former also in the solid state (Adamson, Bell & Shearer, 1982). In contrast, amino derivatives have only one lone pair of electrons and can only associate to form dimers or cyclic oligomers. This has been particularly noted for organoberyllium amino derivatives, where both entropy factors and steric bulk on the donor atom favour the formation of dimers relative to higher associated products, but dimers involve greater valence-angle deformation which may be relieved by the formation of larger cyclic oligomers (Coates & Fishwick, 1967). Aminozinc alkyls are all dimers in benzene solution (Coates & Ridley 1965), as are the ketimino derivatives RZnN=CPh (Pattison & Wade, 1968), and to confirm the existence of three-coordinate zinc in the solid state we have determined the structure of methyl-(diphenylamino)zinc.

Experimental. Preparation by heating freshly sublimed diphenylamine and dimethylzinc under nitrogen in a

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sealed tube at 343K, recrystallization from benzene, D_m by flotation, irregular hexagonal plates, crystal $0.13 \times 0.16 \times 0.31$ mm sealed in a glass capillary tube under dry nitrogen, unit-cell dimensions from zero-level precession photographs, Zr-filtered Mo radiation, layers $h0l$ to $h, 13, l$ recorded photographically by the equi-inclination Weissenberg method, Ni-filtered Cu radiation, intensities estimated visually* and the layers placed on a common scale by comparison with photographs on which timed exposures of different nets had been made, 2110 intensities ($h0-9, k0-13, l0-25$), corrected for Lorentz, polarization and absorption (Busing & Levy, 1957), though in view of the value of μ and the small cross section of the crystal these corrections were small. Structure solved by Patterson and Fourier methods, H atoms could not be satisfactorily located; atomic scattering factors from *International Tables for X-ray Crystallography* (1962), least-squares refinement on F , all atoms anisotropic, $R = 0.086$, $R_w = 0.013$ for 2110 observed reflections, $w^{1/2} = [1 - \exp(-20)(\sin\theta/\lambda)^2]^{1/2} / (1 + 0.2|F_o| + 0.0012 \times |F_o|^2 + 0.00003 |F_o|^3)^{1/2}$, unobserved reflections given zero weight,† final difference synthesis showed small peaks at the sites of the Zn, N and C atoms but no other pronounced features, computer programs supplied by Professor D. W. J. Cruickshank and Dr J. Sime of Glasgow University.

Discussion. Final positional parameters and equivalent isotropic temperature factors are given in Table 1.

The arrangement of atoms in the molecule is as shown in Fig. 1 and bond lengths and angles with their e.s.d.'s are listed in Table 2. Although the space group does not impose any symmetry on the molecule, the molecular symmetry is nearly $2/m$. As in solution, the molecule is a dimer and contains a four-membered Zn_2N_2 ring. The N atoms are four-coordinate but the Zn atoms are each bonded to two N atoms and to a methyl C atom and are therefore three-coordinate. This is the first example of three-coordinate zinc to have been established by X-ray structural analysis. The two Zn—C bonds are the same within experimental error with a mean value of 1.948 (17) Å. Although one might expect differences in Zn—C bond lengths for compounds containing Zn having differing coordination numbers, these distances in Me_2Zn (1.94 Å) which contains two-coordinate zinc (Rundle, Olson, Stucky &

Engbretson, 1963), $(MeZnNPh_2)_2$ — three-coordinate zinc [1.948 (17) Å] and $(MeZnOMe)_4$ — four-coordinate zinc [1.946 (28) Å] (Shearer & Spencer, 1980) do not differ significantly. In Me_2Zn , Zn is sp hybridized and in the latter two compounds Zn formally uses sp^2 and sp^3 hybrid orbitals, respectively. In practice the distinction is not so clear cut. In these compounds the necessary bond angles in the four-membered rings involve the use by Zn of orbitals with large p character and consequently the orbitals for bonding to C have greater s character than their formal hybridization states suggest.

Table 1. Fractional positional parameters ($\times 10^5$ for Zn, $\times 10^4$ for C, N) and B_{eq} values with e.s.d.'s in parentheses

Equivalent isotropic temperature factors were calculated by the method of Willis & Pryor (1975).

	x	y	z	B_{eq} (Å ²)
Zn(1)	39073 (18)	5280 (10)	25768 (6)	5.07 (6)
Zn(2)	12508 (18)	18927 (10)	23172 (6)	5.08 (6)
N(1)	2874 (12)	1096 (6)	1738 (4)	4.8 (4)
N(2)	2295 (11)	1332 (6)	3154 (4)	4.5 (4)
C(1)	1760 (13)	481 (7)	1385 (5)	4.6 (4)
C(2)	1842 (14)	386 (8)	701 (5)	5.2 (5)
C(3)	751 (17)	-213 (9)	385 (6)	6.3 (6)
C(4)	-469 (18)	-736 (10)	734 (7)	6.8 (6)
C(5)	-533 (16)	-649 (10)	1403 (7)	6.6 (6)
C(6)	569 (15)	-70 (9)	1723 (5)	5.7 (5)
C(7)	4159 (14)	1558 (8)	1345 (5)	4.9 (4)
C(8)	3926 (16)	2420 (9)	1151 (6)	6.3 (6)
C(9)	5180 (21)	2880 (11)	772 (8)	7.7 (7)
C(10)	6735 (19)	2421 (10)	603 (6)	7.1 (7)
C(11)	7007 (18)	1554 (10)	794 (7)	6.7 (6)
C(12)	5704 (17)	1111 (9)	1175 (6)	6.2 (6)
C(13)	3352 (12)	1950 (7)	3510 (5)	4.7 (4)
C(14)	3263 (15)	2045 (8)	4194 (5)	5.5 (5)
C(15)	4373 (18)	2662 (10)	4503 (6)	6.7 (6)
C(16)	5581 (19)	3154 (10)	4152 (7)	7.2 (7)
C(17)	5685 (17)	3036 (11)	3491 (8)	7.5 (7)
C(18)	4610 (15)	2452 (8)	3178 (6)	5.6 (5)
C(19)	974 (13)	858 (7)	3537 (4)	4.8 (4)
C(20)	1241 (17)	15 (9)	3773 (5)	6.0 (5)
C(21)	5 (19)	-424 (9)	4167 (6)	6.5 (6)
C(22)	-1548 (17)	30 (10)	4325 (6)	6.7 (6)
C(23)	-1848 (17)	874 (10)	4089 (6)	6.7 (6)
C(24)	-602 (15)	1295 (9)	3692 (7)	6.2 (6)
C(25)	5797 (22)	-312 (11)	2756 (9)	8.5 (8)
C(26)	-582 (23)	2788 (13)	2151 (9)	9.1 (9)

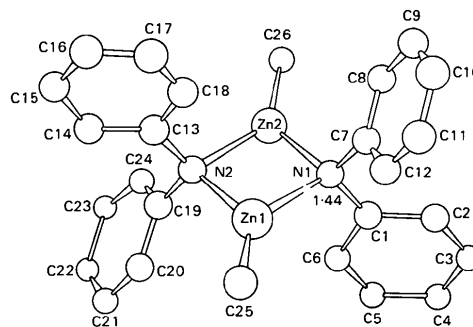


Fig. 1. Structure of $(MeZnNPh_2)_2$.

* The analysis was completed in 1966 before a diffractometer became available at Durham. This paper is part of an effort by Dr Shearer's co-workers to complete the publication of the work he supervised.

† Lists of structure factors, anisotropic thermal parameters, least-squares planes data, short intramolecular distances and atomic coordinates referred to crystal axes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38600 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Zn(1)—C(25)	1.939 (17)	C(8)—C(9)	1.404 (20)
Zn(2)—C(26)	1.957 (18)	C(9)—C(10)	1.406 (21)
Zn(1)—N(1)	2.067 (8)	C(10)—C(11)	1.370 (21)
Zn(1)—N(2)	2.079 (8)	C(11)—C(12)	1.420 (19)
Zn(2)—N(1)	2.081 (9)	C(12)—C(7)	1.390 (17)
Zn(2)—N(2)	2.062 (8)	C(13)—C(14)	1.406 (14)
N(1)—C(1)	1.441 (13)	C(14)—C(15)	1.399 (18)
N(1)—C(7)	1.438 (14)	C(15)—C(16)	1.375 (20)
N(2)—C(13)	1.421 (13)	C(16)—C(17)	1.365 (22)
N(2)—C(19)	1.454 (13)	C(17)—C(18)	1.354 (19)
C(1)—C(2)	1.405 (14)	C(18)—C(13)	1.389 (15)
C(2)—C(3)	1.379 (17)	C(19)—C(20)	1.365 (15)
C(3)—C(4)	1.404 (19)	C(20)—C(21)	1.397 (18)
C(4)—C(5)	1.374 (20)	C(21)—C(22)	1.395 (19)
C(5)—C(6)	1.367 (18)	C(22)—C(23)	1.369 (21)
C(6)—C(1)	1.404 (16)	C(23)—C(24)	1.394 (19)
C(7)—C(8)	1.360 (17)	C(24)—C(19)	1.397 (16)
Zn(2)—N(2)—Zn(1)	89.4 (3)	C(1)—C(2)—C(3)	120.2 (10)
Zn(2)—N(1)—Zn(1)	89.2 (3)	C(2)—C(3)—C(4)	121.2 (11)
N(1)—Zn(2)—N(2)	90.7 (3)	C(3)—C(4)—C(5)	118.4 (12)
N(1)—Zn(1)—N(2)	90.6 (3)	C(4)—C(5)—C(6)	120.9 (12)
C(26)—Zn(2)—N(2)	133.9 (6)	C(5)—C(6)—C(1)	121.8 (11)
C(26)—Zn(2)—N(1)	135.3 (6)	C(6)—C(1)—C(2)	117.4 (10)
C(25)—Zn(1)—N(1)	134.6 (6)	C(7)—C(8)—C(9)	122.5 (12)
C(25)—Zn(1)—N(2)	134.4 (6)	C(8)—C(9)—C(10)	117.5 (14)
Zn(2)—N(2)—C(19)	112.3 (6)	C(9)—C(10)—C(11)	121.2 (13)
Zn(1)—N(2)—C(13)	109.6 (6)	C(10)—C(11)—C(12)	119.5 (13)
Zn(2)—N(1)—C(1)	107.8 (6)	C(11)—C(12)—C(7)	119.8 (12)
Zn(1)—N(1)—C(7)	113.8 (7)	C(12)—C(7)—C(8)	119.4 (11)
Zn(2)—N(2)—C(13)	112.0 (6)	C(13)—C(14)—C(15)	119.1 (10)
Zn(1)—N(2)—C(19)	115.3 (6)	C(14)—C(15)—C(16)	121.1 (12)
Zn(2)—N(1)—C(7)	116.2 (7)	C(15)—C(16)—C(17)	119.0 (14)
Zn(1)—N(1)—C(1)	112.0 (6)	C(16)—C(17)—C(18)	121.1 (14)
C(19)—N(2)—C(13)	115.4 (8)	C(17)—C(18)—C(13)	122.0 (12)
C(1)—N(1)—C(7)	115.0 (8)	C(18)—C(13)—C(14)	117.6 (10)
N(1)—C(1)—C(2)	122.4 (9)	C(19)—C(20)—C(21)	122.6 (12)
N(1)—C(1)—C(6)	120.2 (9)	C(20)—C(21)—C(22)	118.0 (12)
N(1)—C(7)—C(8)	122.0 (10)	C(21)—C(22)—C(23)	120.4 (12)
N(1)—C(7)—C(12)	118.5 (10)	C(22)—C(23)—C(24)	120.5 (12)
N(2)—C(13)—C(14)	123.1 (9)	C(23)—C(24)—C(19)	120.0 (12)
N(2)—C(13)—C(18)	119.2 (9)	C(24)—C(19)—C(20)	118.5 (10)
N(2)—C(19)—C(20)	122.6 (9)		
N(2)—C(19)—C(24)	118.8 (10)		

The four Zn—N lengths are the same within experimental error with a mean value of 2.072 (8) Å. This distance is significantly greater than the value of 2.01 (1) Å observed in bis(imidazole)zinc(II) chloride where Zn is tetrahedral (Lundberg, 1966) but is similar to the distance of 2.09 (2) Å in (thiosemicarbazide)zinc(II) chloride where Zn is four-coordinate but both it and N are part of a five-membered ring (Cavalca, Nardelli & Branchi, 1960). This distance also closely agrees with the Zn—O distance [2.078 (15) Å] in (MeZnOMe)₄. As a net result of the difference in size of the two donor atoms and change in hybridization state of the metal, the Zn—O and Zn—N bond lengths become almost equal. As with (MeZnOMe)₄, it is difficult to correlate the observed bond lengths with the tetrahedral covalent radii. The Zn—C length is very much shorter than the covalent radii sum (2.08 Å) (Pauling, 1960), the Zn—N length much longer, similar to the effect noted in (MeZnOMe)₄ (Shearer & Spencer, 1980). Although some increase in Zn—N and Zn—O lengths over predicted values is expected in view of the valence angles and the polar character of the Zn—O and Zn—N bonds in the rings, it is not clear why the Zn—C lengths should be so much shorter than the value derived from the covalent radii.

All four C—N lengths are the same within experimental error and the mean value of 1.438 (13) is as expected. Though none of the C—C—C angles differ significantly from the mean value of 119.9 (12)° in each of the four cases, the value of the ring angle at C bonded to N is less than 120° as in (Ph₃Al)₂ (Malone & McDonald, 1967). The mean C—C bond length, 1.39 (2) Å, is close to that of benzene, 1.397 Å, none of the individual values differing significantly from the mean. The mean Zn—N—Zn and N—Zn—N angles are respectively 89.3 (3) and 90.6 (3)°, the individual values agreeing closely. The difference between these two mean values is considered significant. In (MeZnOMe)₄ the angles at Zn deviate more from the tetrahedral value than those at O; however, in (MeZnNPh₂)₂, Zn is formally *sp*² hybridized, N *sp*³ and the combined effect results in a situation in which the angles at Zn are only slightly greater. Since the Zn—N—Zn angles are approximately 90°, the other angles at N are considerably greater than tetrahedral. This increase is greatest in the case of the C—N—C angles which have a mean value of 115.2 (8)°. In this way the separations between atoms in adjacent phenyl groups are made as large as possible. Of the eight N—C—C angles, N(2)—C(13)—C(14) is 123.1 (9)° and this is formally greater than the expected value of 120°. Increase in this angle increases the separation of C(14) from the phenyl group C(19)—(24). The related angle N(1)—C(1)—C(2) has a value of 122.4 (9)° but in this case the difference from 120° is not significant.

With the exception of the C(19)—(24), N(2) group, where the deviation from planarity is considered significant at the 0.1% probability level, the other three phenyl groups are considered to be planar.* The planes of the two phenyl rings bonded to the same N atom are in both cases almost perpendicular to each other. The dihedral angle between the mean planes through C(1)—(6) and C(7)—(12) is 81.1 (11)°. The corresponding value for the phenyl groups attached to N(2) is 83.0 (12)°. The two *cis* phenyl rings which are bonded to different N atoms are also approximately perpendicular, values of the dihedral angles being 84.0 (12) [for C(1)—(6) and C(19)—(24)] and 80.1 (14)° [C(7)—(12) and C(13)—(18)]. These angles are similar to those found between phenyl rings attached to phosphorus in phenyltriphosphonitriles (Mani, Ahmed & Barnes, 1966) where the environment of P is similar to that of N in (MeZnNPh₂)₂. The dihedral angles between the best plane through the Zn—N ring and the planes of the phenyl groups C(1)—(6) and C(13)—(18) are 90° within experimental error. This equalizes the contacts between the two Zn atoms and C(6) and similarly those with C(18). The dihedral angle between the plane of the ring and the planes of the phenyl groups C(7)—(12) and C(19)—(24) are 55.9 (11) and 54.1 (11)°, respectively.

* The results of mean-plane calculations have been deposited. See deposition footnote.

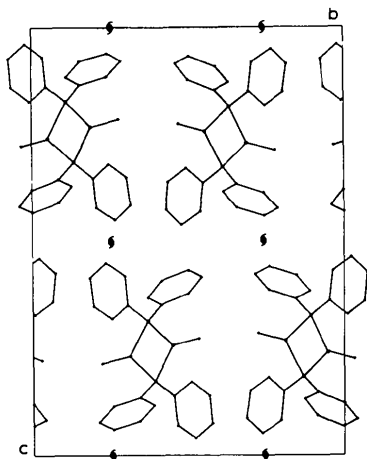


Fig. 2. $(\text{MeZnPh}_2)_2$ —projection on (100).

The two methyl C atoms are each involved in only one intramolecular contact less than 4 Å, of which that between C(25) and C(12) has a value of 3.87 (4) Å.* The contact involving C(26) is seen to be given by inverting C(25)···C(12) through the molecular centre and has a similar value. All other short intramolecular contacts are between C atoms in adjacent phenyl groups. There are several contacts less than 3.7 Å and two have values of *ca* 2.8 Å. Although this latter distance is less than the sum of the van der Waals radii, it is not considered unusual in a molecule which contains two phenyl groups bonded to a common atom. Again, the pairs of contacts between atoms approximately related to each other by inversion through the molecular centre are similar in value. The packing arrangement is shown in Fig. 2. All approach distances are > 3.7 Å so that there does not appear to be any significant interaction between molecules. Thus there is no possibility of further association through methyl bridges so $(\text{MeZnNPh}_2)_2$ remains a dimer in the crystal and Zn forfeits the coordination number four preferred in its organic compounds. The structural evidence available indicates that methyl bridges normally involve very sharp bridge angles of *ca* 70°. In the case of Zn,

* A list of intramolecular non-bonded contact distances has been deposited. See deposition footnote.

with a tetrahedral covalent radius of 1.31 Å (Pauling, 1960) this would force the metal atoms closer together than the Zn—Zn single-bond distance and would lead to inner-core repulsions (Rundle, 1963). So for the same reason that Me_2Zn does not form a polymer like Me_2Be (Snow & Rundle, 1951), $(\text{MeZnNPh}_2)_2$ remains a dimer in the crystal.

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