

# Molecular Structures of Bis(3-(Dimethylamino)propyl)zinc, $\text{Zn}[(\text{CH}_2)_3\text{N}(\text{CH}_3)_2]_2$ , by X-ray and Gas Electron Diffraction and Bis(3-mercaptopropyl)zinc, $\text{Zn}[(\text{CH}_2)_3\text{SCH}_3]_2$ , by Gas Electron Diffraction

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The molecular structures of  $\text{Zn}[(\text{CH}_2)_3\text{N}(\text{CH}_3)_2]_2$  (III) and  $\text{Zn}[(\text{CH}_2)_3\text{SCH}_3]_2$  (II) have been determined by X-ray crystallography (III) and gas electron diffraction (II and III). The chelating nature of the ligands is confirmed. Crystals of  $\text{C}_{10}\text{H}_{24}\text{N}_2\text{Zn}$  are orthorhombic of space group  $Fdd2$  with  $a = 1704.4$  (1) pm,  $b = 2473.4$  (2) pm,  $c = 610.8$  (1) pm, and  $Z = 8$ . The structure was refined to  $R = 0.034$  for 732 observed reflections. In the crystalline phase, the molecular symmetry of III is  $C_2$  and the Zn-N bond distance is 230.7 (4) pm. The coordination around Zn is considerably distorted from tetrahedral:  $\angle\text{CZnC} = 156.4$  (2)° and  $\angle\text{NZnN} = 109.7$  (1)°. In the gas phase the Zn-N bond distance has increased by 8 or 9 pm to 239.2 (15) pm. The Zn-S bond distance in II is 273.2 (12) pm, and the  $\angle\text{SZnS}$  angle is very large, 173 (12)°. The coordination geometry around zinc is consequently nearly square-planar. The Zn-N and Zn-S electron donor-acceptor bonds are 30-40 pm longer than the sum of the "tetrahedral covalent" radii. The very large vibrational amplitudes,  $l(\text{Zn-N}) = 17$  (3) pm and  $l(\text{Zn-S}) = 13$  (2) pm, also attest to the weakness of the interaction.

Diorganozinc compounds interact with electron donors like ethers or tertiary amines, but donor-acceptor bonds are clearly weaker than in complexes of triorganoaluminum or -gallium compounds:<sup>1</sup> well-defined complexes between diorganozinc compounds and dialkyl ethers have never been characterized. Interaction with cyclic ethers is stronger, but complexes with tetrahydrofuran are at least 90% dissociated in the gas phase at 140 °C.<sup>2</sup> Electron donor-acceptor bonds between Zn and N are generally stronger than bonds between Zn and O, but we have nevertheless found that the electron diffraction pattern of the gas formed by evaporation from a liquid sample of composition corresponding to the complex  $(\text{CH}_3)_2\text{Zn-N}(\text{CH}_3)_3$  indicated quantitative dissociation to  $(\text{CH}_3)_2\text{Zn}$  and  $\text{N}(\text{CH}_3)_3$  at 30 °C.<sup>3</sup> Perhaps because of the weakness of the interaction, structural information on complexes of diorganozinc compounds with amines, ethers, or thioethers has not been available.

Both Thiele and co-workers<sup>4,5</sup> and we<sup>6</sup> have synthesized a series of long-chain organozinc compounds with a donor atom in the  $\delta$ - or  $\epsilon$ -position on the chain:  $\text{Zn}[(\text{CH}_2)_3\text{OCH}_3]_2$  (I),<sup>6</sup>  $\text{Zn}[(\text{CH}_2)_3\text{SCH}_3]_2$  (II),<sup>6</sup>  $\text{Zn}[(\text{CH}_2)_3\text{N}(\text{CH}_3)_2]_2$  (III),<sup>5,6</sup> and  $\text{Zn}[(\text{CH}_2)_4\text{OCH}_3]_2$  (IV).<sup>4,6</sup> These compounds are monomeric in benzene and do not appear to interact with ethers. These observations suggest that the chains are

coiled back to allow formation of donor-acceptor bonds between the donor atoms and zinc, as indicated for II and III in Figures 1 and 2.

Conclusive evidence for intramolecular coordination and the double chelate structures was provided by the <sup>13</sup>C NMR spectra,<sup>6</sup> and the results of microwave titrations with 2,2'-bipyridine<sup>6</sup> indicate that the strength of the donor-acceptor bond decreases along the series III > I > II > IV.

We have recently published the structures of I and IV as determined by gas electron diffraction (GED).<sup>7</sup> In this paper we publish the structure of III determined by both X-ray crystallography and GED and the structure of II determined by GED.

## Experimental Section

Samples of  $\text{Zn}[(\text{CH}_2)_3\text{SCH}_3]_2$  (II) and  $\text{Zn}[(\text{CH}_2)_3\text{N}(\text{CH}_3)_2]_2$  (III) were synthesized and characterized as described earlier.<sup>6</sup> Crystals of III suitable for X-ray analysis were obtained by crystallization from a *n*-pentane solution at -50 °C.

**X-ray Study of III.** X-ray data were collected on an Enraf-Nonius CAD4F diffractometer for a colorless transparent crystal of III, mounted in a Lindemann glass capillary. Crystal data and numerical details of the structure determination are given in Table I. Lattice parameters with standard deviations were determined from the  $\theta$  values of 16 reflections ( $5 < \theta < 15^\circ$ ). The observed extinctions indicated space group  $Fdd2$ . Standard deviations in the intensities, based on counting statistics ( $\equiv \delta_{\text{cs}}(I)$ ), were increased according to an analysis of the variance of the reference reflections:<sup>8</sup>  $\sigma^2(I) = \sigma_{\text{cs}}^2(I) + (0.018 I)^2$ . The reflection set was corrected for  $L_p$ , a small linear decay of 2% (during 20 h of X-ray exposure time), and absorption (DIFABS;<sup>9</sup> minimum

(1) Boersma, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, 830.

(2) Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1982**, *319*, 183.

(3) Boersma, J.; Dekker, J.; Haaland, A.; Hougen, J. unpublished results.

(4) Thiele, K.-H.; Heinrich, M.; Brüser, W.; Schröder, S. *Z. Anorg. Allg. Chem.* **1977**, *432*, 221.

(5) Thiele, K.-H.; Langguth, E.; Müller, G. E. *Z. Anorg. Allg. Chem.* **1980**, *462*, 152.

(6) Hofstee, H. K.; Boersma, J.; van der Meulen, J. D.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1978**, *153*, 245.

(7) Boersma, J.; Fernholt, L.; Haaland, A. *Acta Chem. Scand., Ser. A* **1984**, *A38*, 523.

(8) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **1975**, *A31*, 245.

(9) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

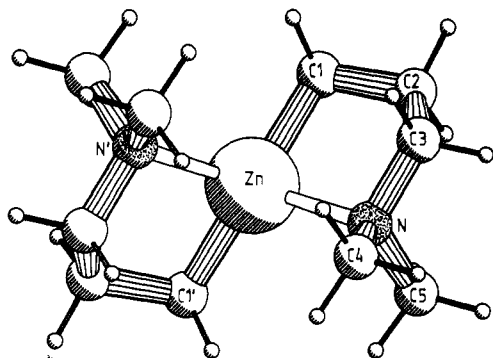


Figure 1. View down the crystallographic twofold axis of the X-ray molecular structure of  $Zn[(CH_2)_3N(CH_3)_2]_2$  with adopted numbering. Primed atoms are related to corresponding unprimed atoms via  $-x, -y, z$ .

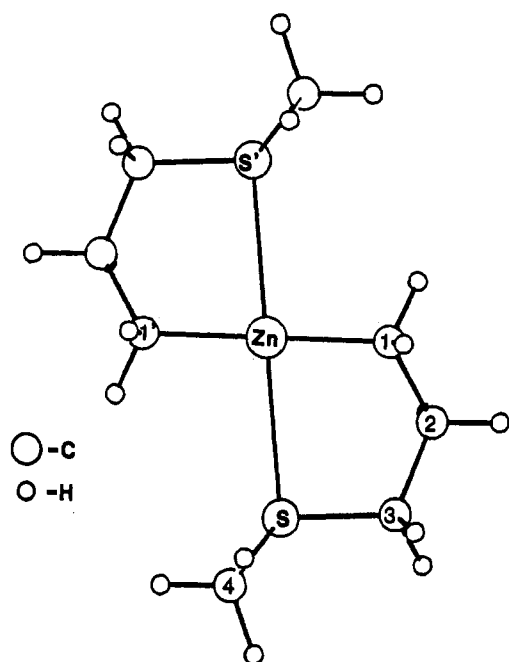


Figure 2. Molecular model of  $Zn[(CH_2)_3SCH_3]_2$ , symmetry  $C_2$ .

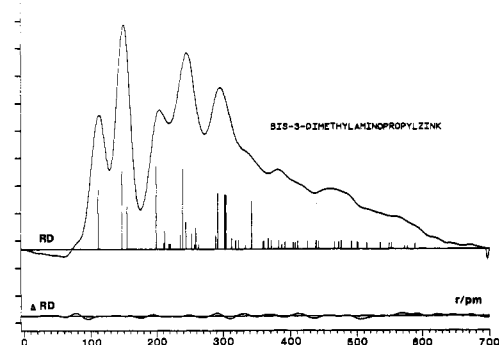


Figure 3. Radial distribution curve for  $Zn[(CH_2)_3N(CH_3)_2]_2$ . Major interatomic distances are indicated by bars of height approximately equal to the area under the corresponding peak. Below: difference curve. Artificial damping constant  $k = 20 \text{ pm}^2$ .

and maximum corrections = 0.83 and 1.13, respectively). The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares on  $F$  with SHELX76.<sup>10</sup> Hydrogen atoms were introduced on calculated positions and refined with fixed geometry ( $C-H = 108 \text{ pm}$ ) to the carbon atoms they are attached to with one overall isotropic temperature parameter ( $U = 0.105(6) \times 10^4 \text{ pm}^2$ ). The absolute structure was

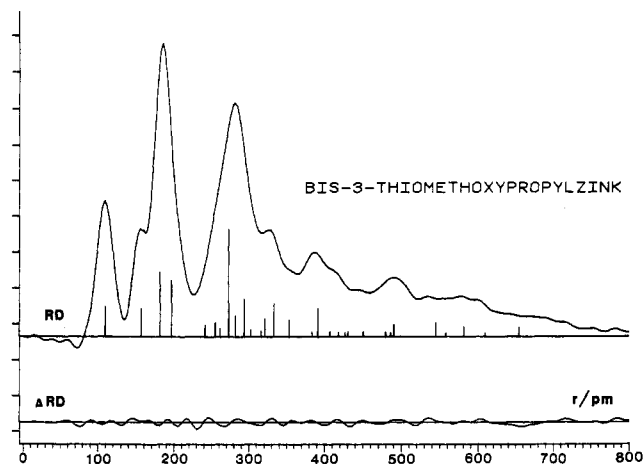


Figure 4. Radial distribution curve for  $Zn[(CH_2)_3SCH_3]_2$ . Major interatomic distances are indicated by bars of height approximately equal to the area under the corresponding peak. Below: difference curve. Artificial damping constant  $k = 20 \text{ pm}^2$ .

Table I. Crystal Data and Details of the Structure Determination

(a) Crystal Data	
formula	$C_{10}H_{24}N_2Zn$
mol wt	237.69
cryst syst	orthorhombic
space group	$Fdd2$ (No. 43)
$a$ , pm	1704.4 (1)
$b$ , pm	2473.4 (2)
$c$ , pm	610.8 (1)
$V$ , $\text{nm}^3$	2.5749 (5)
$Z$	8
$D(\text{calcd})$ , $\text{g cm}^3$	1.226
$F(000)$ , electrons	1024
$\mu(\text{Mo K}\alpha)$ , $\text{cm}^{-1}$	19.2
cryst size, mm	$0.25 \times 0.25 \times 0.75$
(b) Data Collection	
$\theta_{\min}, \theta_{\max}$ , deg	1.65, 30
radiatn, pm	Mo $K\alpha$ (Zr-filtered), 71.073
$\omega/2\theta$ scan, deg	$1.00 + 0.35 \tan \theta$
hor, vert apert, dist to cryst, mm	3, 5, 173
ref refls (rmsd)	3,3,1 (0.97%); 3,-3,1 (0.60%); -3,3,1 (0.77%); -3,-3,1 (0.69%)
data set	$h, 0:23; k, 0:34; l, 0:8$
total data, unique data	1078, 1020
obsd data ( $I > 2.5\sigma(I)$ )	732
(c) Refinement	
NO, NV, S	732, 66, 1.67
$R, wR$	0.034, 0.030
weighting scheme	$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\text{av}}$	0.05
min and max resd dens., $\text{e pm}^3$	$3.7 \times 10^{-7}$ and $-3.0 \times 10^{-7}$

Table II. Positional and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of  $C_{10}H_{24}N_2Zn^a$

atom	$x$	$y$	$z$	$U_{\text{eq}}$ , $\text{pm}^2$
Zn	0.5 (...)	0.5 (...)	0 (-)	407 (2)
N	0.6052 (2)	0.4763 (1)	0.2173 (7)	480 (10)
C(1)	0.5606 (2)	0.5665 (2)	-0.0665 (8)	530 (10)
C(2)	0.6466 (3)	0.5564 (2)	-0.001 (1)	630 (20)
C(3)	0.6504 (3)	0.5276 (2)	0.218 (1)	660 (20)
C(4)	0.5928 (4)	0.4566 (2)	0.4395 (9)	820 (20)
C(5)	0.6475 (4)	0.4347 (2)	0.091 (1)	720 (20)

<sup>a</sup> Numbers in parentheses are esd's in units of the last digit.  $U_{\text{eq}} = \frac{1}{3} \sum \sum U_{ij} a_i^* a_j^* a_i a_j$ .

determined by refinement with both positive and negative  $f''$  values. Convergence was reached at  $R = 0.034$  for 732 observed reflections and negative  $f''$ . The refined parameters included all positional and anisotropic thermal parameters for the non-hy-

(10) Sheldrick, G. M. SHELX76, a program for crystal structure determination; University of Cambridge: England, 1976.

**Table III. Selected Data on the X-ray Geometry of Zn[(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>3</sub>)<sub>2</sub>] (III)**

Bond Distances (pm)			
Zn-N	230.7 (4)	N-C(5)	147.4 (7)
Zn-C(1)	198.4 (5)	N-C(4)	145.7 (7)
N-C(3)	148.4 (6)	C(1)-C(2)	154.0 (6)
		C(2)-C(3)	151.7 (8)
Bond Angles (deg)			
N-Zn-C(1)	85.6 (1)	Zn-N-C(4)	120.5 (3)
N-Zn-N'	109.7 (1)	C(3)-N-C(5)	110.1 (4)
N-Zn-C(1')	108.2 (1)	C(3)-N-C(4)	111.0 (4)
N'-Zn-C(1)	108.2 (1)	C(4)-N-C(5)	109.0 (4)
C(1)-Zn-C(1')	156.4 (2)	Zn-C(1)-C(2)	107.9 (3)
Zn-N-C(3)	100.8 (3)	C(1)-C(2)-C(3)	110.2 (4)
Zn-N-C(5)	104.9 (3)	N-C(3)-C(2)	112.1 (4)
Torsion Angles (deg)			
C(1)-Zn-N-C(3)	10.2 (3)	N-Zn-C(1)-C(2)	17.0 (3)
Zn-C(1)-C(2)-C(3)	-42.9 (5)	Zn-N-C(3)-C(2)	-36.6 (4)
C(1)-C(2)-C(3)-N	56.0 (5)		

<sup>a</sup> Atoms related by the symmetry relation  $-x, -y, z$  to the basic unit are indicated with a prime.

drogen atoms. Positional parameters and equivalent isotropic temperature factors for the non-hydrogen atoms are listed in Table II. Scattering factors were taken from Cromer and Mann<sup>11</sup> and anomalous dispersion terms from Cromer and Liberman.<sup>12</sup> Geometrical calculations were done with PLATO.<sup>13</sup>

**Gas Electron Diffraction.** The GED patterns were recorded on Balzers Eldigraph KDG-2 with nozzle temperatures of about 105 (II) and 85 °C (III). Exposures were made with nozzle-to-plate distances of 50 and 25 cm. Five or six plates from each set were photometered and the optical densities processed by standard procedures. The molecular intensity curves obtained for each nozzle-to-plate distance were averaged, but not connected. The curves extended from  $s = 20$  to  $s = 145 \text{ nm}^{-1}$  with increment  $\Delta s = 125 \text{ nm}^{-1}$  (50 cm) and from  $s = 40$  to  $s = 280 \text{ nm}^{-1}$  with increment  $\Delta s = 250 \text{ nm}^{-1}$  (25 cm).

The complex atomic scattering factors,  $f'(s)$ , were calculated from an analytical representation of the atomic potential,<sup>14</sup> using a program written by Yates.<sup>15</sup> The molecular intensities were modified by multiplication with  $s/|f'_C||f'_{Zn}|$ .

Structure analysis of III was based on a model of  $C_2$  symmetry as found in the crystalline phase and shown in Figure 1. Structure refinement of II was based on a  $C_2$  model as shown in Figure 2. In order to reduce the number of parameters to be refined, we made the following additional assumptions for each molecule: (i) all C-C bonds are equal; (ii) all C-N (or C-S) bonds are equal; (iii) all C-H bonds are equal; (iv) all  $\angle\text{CCC}$  angles are equal; (v) the NCH<sub>3</sub> (and SCH<sub>3</sub>) fragments have  $C_{3v}$  symmetry with  $\angle\text{NCH} = \angle\text{SCH} = 110^\circ$ ; (vi) the  $\angle\text{HCH}$  valence angles of the methylene groups were fixed at  $106^\circ$ , and the plane defined by the group was assumed to bisect the opposite angle; for III it was further assumed that (vii) the valence angles  $\angle\text{C(3)NC(4)}$  and  $\angle\text{C(3)NC(5)}$  are equal.

After these assumptions have been made, the molecular structure of II is determined by 13 independent parameters, i.e. the bond distances Zn-C, C-C, C-H, and C-D, (D = donor atom = S or N), the valence angles  $\angle\text{CZnC}$ ,  $\angle\text{ZnCC}$ ,  $\angle\text{CCC}$ ,  $\angle\text{CCD}$ , and  $\angle\text{C(3)DC(4)}$ , and the torsion angles  $\tau(\text{C(1')ZnC(1)C(2)})$ ,  $\tau(\text{ZnC(1)C(2)C(3)})$ ,  $\tau(\text{C(1)C(2)C(3)D})$ , and  $\tau(\text{C(2)C(3)DC(4)})$ .

The molecular structure of III is determined by the same 13 parameters plus the dihedral angle  $\tau(\text{C(2)C(3)DC(5)})$ . The 14 structure parameters, four root-mean-square amplitudes of vibration, and two scale factors were refined by least-squares calculations on the modified molecular intensity curves, under the constraints of a geometrically consistent  $r_\sigma$  structure.<sup>16</sup> Those

**Table IV. Structure Parameters of Zn[(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>3</sub>)<sub>2</sub>] (III) and Zn[(CH<sub>2</sub>)<sub>3</sub>SCH<sub>3</sub>] (II) Obtained by Gas Electron Diffraction<sup>a</sup>**

	III, D = N	II, D = S
Bond Distances (pm)		
Zn-C	199.1 (6)	196.6 (6)
Zn-D	239.2 (15)	273.2 (12)
C-C	154.7 (8)	156.0 (8)
C-D	146.7 (3)	181.3 (5)
C-H	110.7 (3)	109.6 (5)
Valence Angles (deg)		
$\angle\text{CZnC}$	152 (8)	163 (15)
$\angle\text{DZnD}$	117 (4)	173 (12)
$\angle\text{DZnC(1)}$	82 (2)	85 (2)
$\angle\text{DZnC(1')}$	113 (4)	96 (2)
$\angle\text{ZnCC}$	110 (2)	113 (3)
$\angle\text{CCC}$	104 (3)	112 (3)
$\angle\text{CCD}$	114 (3)	115 (2)
$\angle\text{C(3)DZn}$	101 (2)	91 (2)
$\angle\text{C(3)DC(4)}$	112 (2)	112 (5)
Torsion Angles <sup>b</sup> (deg)		
$\tau(\text{ZnC(1)C(2)C(3)})$	-53	-55
$\tau(\text{C(1)C(2)C(3)D})$	58	52
$\tau(\text{C(2)C(3)DZn})$	34	24
$\tau(\text{C(3)DZnC(1)})$	3	3
$\tau(\text{DZnC(1)C(2)})$	27	30
$\tau(\text{C(2)C(3)DC(4)})$	-167	-144
$\tau(\text{C(2)C(3)DC(5)})$	73	
$\tau(\text{C(1')ZnC(1)C(2)})$	-98	124
Vibrational Amplitudes (pm)		
Zn-C	7.3 (6)	6.3 (9)
Zn-D	17 (3)	13 (2)
C-C	(5.4)	6.6 (8)
C-D	(5.2)	(5.5)
C-H	7.1 (5)	7.6 (7)

<sup>a</sup> Estimated standard deviations in parentheses in units of the last digit. D = donor atom = N or S. <sup>b</sup> The dihedral angles are not unique. Estimated standard deviations obtained for the values listed range from 6 to 8°.

amplitudes that could not be refined were fixed at values that appeared reasonable in comparison with the published amplitudes of diethylzinc,<sup>17</sup> dipropylzinc,<sup>17</sup> normal butane,<sup>18</sup> and trimethylamine.<sup>19</sup> When start parameters were taken from the crystal structure, the refinement converged to the values listed in Table IV.

The 13 structure parameters of II were refined along with eight amplitudes of vibration and two scale factors. When start values for torsional angles were taken from the oxygen analogue I,<sup>7</sup> the refinement converged to the values listed in Table IV.

When refining the oxygen compounds I and VI, we found that refinements with different start values would converge to different stable least-squares minima. The various "best models" thus obtained had very similar values for bond distances and valence angles, but there were significant differences between the dihedral angles. Similarly several least-squares minima with different torsional angles were found for III. Since we cannot claim that torsional angles are unique, they are listed without error limits. Estimated standard deviations of other parameters have been expanded by a factor of 3 to include systematic errors and the uncertainty due to non-refined parameters.

## Discussion

In agreement with the conclusions reached by Hofstee and co-workers<sup>6</sup> and in agreement with our work on the oxygen compounds I and IV,<sup>7</sup> we find that the hydrocarbon

(11) Cromer, D. T.; Mann, J. B. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

(12) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(13) Spek, A. L. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon: Oxford, 1982; p 528.

(14) Strand, T. G.; Bonham, R. A. *J. Chem. Phys.* **1964**, *40*, 1686.

(15) Yates, A. C. *Comput Phys. Commun.* **1971**, *2*, 175.

(16) Seip, H. M.; Strand, T. G.; Stølevik, R. *Chem. Phys. Lett.* **1967**, *3*, 617. See also: Gundersen, G. "Annual Report of the Norwegian Electron Diffraction Group", Oslo, 1977.

(17) Almenningen, A.; Helgaker, T. U.; Haaland, A.; Samdal, S. *Acta Chem. Scand.* **1982**, *A36*, 159.

(18) Fitzwater, S.; Bartell, L. S. *J. Am. Chem. Soc.* **1976**, *98*, 8336.

(19) Beagley, B.; Hewitt, T. G. *Trans. Faraday Soc.* **1968**, *64*, 2561.

chains of II and III are coiled back to allow the donor atom D (= S or N) to coordinate to the Zn atom.

The orthorhombic unit cell of III contains eight discrete molecules (Figure 1) that are located on crystallographic twofold axes. Data on the geometry are assembled in Table III. The five-membered chelate ring is significantly puckered with Cremer and Pople<sup>20</sup> puckering parameter values  $Q = 44.3$  (5) pm and  $\phi = 275.2$  (5)°. This corresponds to a half-chair conformation with a pseudo twofold axis running through Zn and the center of the opposing C(2)–C(3) bond. This analysis is consistent with the value 6.6 (4)° for the corresponding asymmetry parameter  $\Delta C_2$  as defined by Duax, Weeks, and Rohrer.<sup>21</sup> The C(4) methyl group takes an equatorial position with respect to the chelate ring and the C(5) methyl an axial position. The same conformation appears to persist in the gas phase, but the presence of other conformers cannot be ruled out.

Although no thermodynamic data on the dissociation energies of diorganozinc complexes are available, a rough estimate of the strengths of zinc–heteroatom dative bonds can be made. Amines are probably the strongest ligands for organozinc compounds. The coordination sphere around zinc in the hypothetical complex  $Me_2Zn \cdot (NMe_3)_2$  would be sterically and electronically equivalent to that in III, so similar complexation energies would be expected. However, the former complex does not exist, and even the known monoligand complex  $Me_2Zn \cdot NMe_3$  is completely dissociated in the gas phase.<sup>3</sup> Apparently the entropy increase on dissociation outweighs the loss of complexation energy. Since the entropy contribution of gaseous  $Me_3N$  to the free energy of dissociation may be estimated to be about 60 kJ/mol, the complexation energy for the first molecule of  $Me_3N$  must be less than 60 kJ/mol and that of the second one even smaller. Since in internally coordinated organozinc compounds dissociation of the ligand will result in only a very minor increase in entropy, even very small complexation energies—maybe down to a few kilojoules per mole—will suffice to keep the internal donor groups coordinated to the metal. It should be realized that weak interactions generally result in flat potential energy surfaces, which means that in these cases large distortions can occur in response to small steric or electronic effects.

The weakness of the electron donor–acceptor bonds is clearly revealed in the bond distances Zn–N = 230.7 (4) pm in III in the solid phase, Zn–N = 239 (2) pm in the gas phase, Zn–O = 237 (2) pm in I, and Zn–S = 273 (1) pm in II: addition of Paulings “tetrahedral covalent radii”<sup>22</sup> yields the bond distances Zn–N = 201 pm, Zn–O = 197 pm, and Zn–S = 235 pm. The softness of the interactions is also demonstrated by the large Zn–D vibrational amplitudes  $l(Zn-N) = 17$  (3) pm,  $l(Zn-O) = 16$  (3) pm (in I),<sup>7</sup> and  $l(Zn-S) = 13$  (2) pm. In contrast the Zn–C amplitudes are 6 or 7 pm; a doubling of the vibrational amplitude corresponds to a reduction of the force constant by a factor of  $1/4$ . In this context it does not seem unreasonable that the Zn–N bonds in III are 8 or 9 pm shorter in the solid state than in the gas phase.

The valence angles around Zn are determined with very wide error limits. The coordination appears to be considerably distorted from tetrahedral: the  $\angle CZnC$  angles in the four compounds range from 150 to 175°. The  $\angle DZnD$  angles in I, II, and IV are not significantly different from 110°, but the  $\angle SZnS$  angle in II is 173 (12)°. In

diorganozinc compounds, both the steric interactions between the organic groups and the electronic energy will be insensitive to small variations in the C–Zn–C angle,<sup>23</sup> so the introduction of additional ligands can easily result in small deviations from linearity. If these additional ligands are very weak (e.g., SMe), there will be no electronic preference for donation in either of the two different p orbitals.<sup>24</sup> Therefore, in compound II, the most favorable arrangement will have the two Zn–S dipoles in an opposing orientation,<sup>25</sup> resulting in a (nearly) square-planar surrounded zinc. With stronger donor ligands, a linear D–Zn–D arrangement will become unfavorable and angles in the vicinity of 90° are to be expected. Because of steric factors and the unfavorable arrangement of the bond dipoles, the actual angle will be slightly larger, but the structure of, e.g.,  $Zn[(CH_2)_3OMe]_2$  (I) is easily understood.

In the  $NMe_2$  complex III, steric factors become important. Given a linear C–Zn–C skeleton and a ligand “bite angle” of about 90°, we are left with two “nonbonded”  $Me_2N$  to  $\alpha-CH_2$  repulsions that also span angles at zinc of only 90°. These repulsions will result in bending of the C–Zn–C axis as discussed above. This bending should be regarded as a steric rather than an electronic effect. A similar effect appears to be present in the  $Ph_2P$ -substituted compound which will be reported soon.<sup>26</sup>

**Electron Donor–Acceptor Bonds to Zinc.** When discussing the length or strength of bonds between electron donors and Zn (“dative bonds”), it is necessary to consider the number and nature of the ligands bonded to zinc through covalent electron pair bonds (one-electron ligands, X), the number and nature of the donor ligands (two-electron ligands, D), the coordination number of the metal, and the net charge of the complex. In the following we restrict our attention to neutral complexes of type  $X_2ZnD_2$  where the coordination number of Zn is 4.

Complexes I–IV may be considered prototypes for the complexes  $R_2ZnD_2$  where R = alkyl and D = N, O, or S. Exchange of one alkyl group for a more electronegative group like chlorine or a transition-metal-containing group leads to a shortening of the dative bond by about 10 pm: in pentadienylzinc chloride–tetramethylethylenediamine<sup>27</sup> and in (3-dimethylamino)propylzinc–tungsten cyclopentadienyl tricarbonyl,<sup>28</sup> the Zn–N distances are 2.15/2.16 and 2.19 Å, respectively. Exchange of the second alkyl group by an electronegative group leads to further shortening of the Zn–D bonds: in the 1:1 complexes of  $ZnCl_2$  with 1,10-phenanthroline<sup>29</sup> and 2,9-dimethylphenanthroline,<sup>30</sup> where the metal coordination is  $Cl_2ZnN_2$ ,

(23) With the assumption of a simple cos dependence between the total bond energy and the C–Zn–C angle, a deformation of 24° is estimated to cost less than 22 kJ/mol [the normal Zn–C covalent bond strength is ca. 170 kJ/mol kcal/mol].

(24) Small donations into the same orbital are—to a first approximation—additive. With increasing strength of electronic interaction, the additivity relation breaks down because of saturation effects. Therefore, two weak ligands can donate to the same or different orbitals, but stronger ligands will have a definite preference for donation into different orbitals.

(25) The SMe ligand will have less steric problems in a square-planar surrounding than the OMe ligand. In normal ether complexes, the ether–oxygen has a trigonal surrounding, which causes the oxygen-bound methyl group to point in the direction of the  $\alpha$ -methylene group of the second ligand. The thioether complex has a pyramidally surrounded sulfur atom that can point its methyl group away from the neighboring  $\alpha$ -methylene group.

(26) Dekker, J.; Boersma, J.; Spek, A. L., to be submitted for publication.

(27) Yasuda, H.; Ohnuma, Y.; Nakamura, A.; Kai, Y.; Yasuoka, N.; Kasui, N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1101.

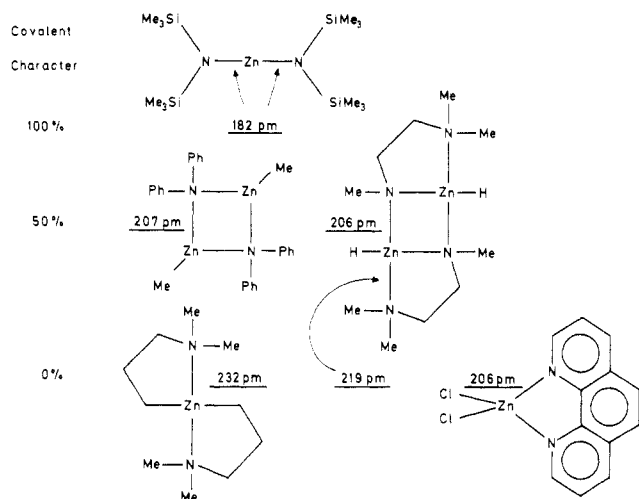
(28) Budzelaar, P. H. M.; Alberts-Jansen, H. J.; Mollema, K.; Boersma, J.; Van der Kerk, G. J. M.; Spek, A. L.; Duisenberg, A. J. M. *J. Organomet. Chem.* **1983**, *243*, 137.

(29) Reimann, C. W.; Block, S.; Perloff, A. *Inorg. Chem.* **1966**, *5*, 1185.

(20) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.

(21) Duax, W. L.; Weeks, C. M.; Rohrer, D. C. *Top. Stereochem.* **1976**, *9*, 271–273.

(22) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Press: Ithaca, NY, 1960; p 246.



**Figure 5.** Some representative Zn-N bond distances.

the mean Zn-N distances are 206 and 207 pm, respectively, about 25 pm shorter than that in  $R_2ZnN_2$ ; in the complex of  $Cl_2Zn$  with thiourea,<sup>31</sup> where metal coordination is  $Cl_2ZnS_2$ , the mean Zn-S distance is 235 pm, about 35 pm shorter than that in  $R_2ZnS_2$ ; in the 1:2 complex of  $Cl_2Zn$  with 1,4-dioxane,<sup>32</sup> where metal coordination is the distorted  $Cl_2ZnO_2$ , the mean of the two Zn-O distances is 215 pm, about 20 pm shorter than that in  $R_2ZnO_2$  (in addition there is a third Zn...O contact at 265 pm); finally, in the 1:2 complex of  $(ArO)_2Zn$  with THF,<sup>33</sup> Ar = 2,6-di-*tert*-butylphenyl, the dative Zn-O(THF) distances are 208 pm, about 30 pm shorter than that in  $R_2ZnO_2$ .

The latter complex also affords a *covalent* Zn-O bond distance, Zn-O(Ar) = 189 pm, 19 pm shorter than the dative Zn-O(THF) distances and about 50 pm shorter than the dative Zn-O distances in  $R_2ZnO_2$ .

A reasonable value for a *covalent* Zn-N bond is provided by the monomeric amide  $Zn[N(SiMe_3)_2]_2$ ,<sup>34</sup> viz., Zn-N = 182 pm, 25 pm shorter than the dative Zn-N bond distance in the  $Cl_2ZnN_2$  complexes and 50 pm shorter than the

dative bond distances in  $R_2ZnN_2$ .

Dative (electron donor-acceptor) bonds to Zn are therefore longer, often considerably longer, than corresponding covalent bonds and are extremely sensitive to inductive effects. Similar conclusions have been reached regarding dative bonds to Ga and Al.<sup>35</sup>

**Zn-N Distances in Dimeric Amides.** The four Zn-N bond distances in the central four-membered ring of  $Me_2Zn_2(\mu-NPh_2)_2$ <sup>36</sup> are 207 pm. See Figure 5. Each bond may be regarded as a 50:50 resonance between covalent and dative bonds, and it is gratifying that the bond distance is close to the mean of the covalent Zn-N distance in  $Zn[N(SiMe_3)_2]_2$  and the dative bond distance in  $R_2ZnN_2$ .

The structure of  $[HZnN(Me)C_2H_4NMe_2]_2$ <sup>37</sup> is also indicated in Figure 5. The bond distances in the central  $Zn_2N_2$  ring are 206 pm and may again be described as having 50% covalent character. The Zn-N distances external to the central ring are 219 pm and may be described as 100% dative. The shortening relative to  $R_2ZnN_2$  may be ascribed to an inductive effect.

In conclusion we believe that Zn-N bond distances in these and more complicated complexes may be rationalized in terms of percent covalent character and inductive effects due to ligand electronegativities. The resulting Zn-N distances span the wide range from 182 to 232 pm.

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**Supplementary Material Available:** Tables of thermal parameters and positional parameters for the hydrogen atoms (1 page); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

(30) Preston, H. S.; Kennard, C. H. L. *Chem. Commun.* 1967, 708.

(31) Kunchur, N. R.; Truter, M. J. *Chem. Soc.* 1958, 3478.

(32) Boardman, A.; Small, R. W. H.; Worrall, I. J. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* 1983, C39, 1005.

(33) Geerts, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* 1986, 25, 1803.

(34) Haaland, A.; Hedberg, K.; Power, P. P. *Inorg. Chem.* 1984, 23, 1972.

(35) Haaland, A. In *Stereochemical Applications of Gas-Phase Electron Diffraction*; Hargittai, I., Ed.; VCH: Deerfield Beach, FL, in press.

(36) Bell, N. A.; Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* 1983, C39, 1182.

(37) Bell, N. A.; Moseley, P. T.; Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1980, B36, 2950.