

Invited review

## Structural analyses of organozinc compounds

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### Abstract

Structures of organozinc compounds determined by X-diffraction, have been reviewed. Almost forty organozinc compounds are surveyed in this review. There are examples of bi-, tri-, tetra-, penta-, hepta- and polynuclear derivatives. Relationship between structural parameters, covalent radii of coordinated atoms and the geometry of the coordination sphere are discussed.

### 1. Introduction

The chemistry of zinc compounds has been extensively investigated, and the relationship between structure and biomedical activity is of major importance. Over the last 20 years, studies on the reactivities of various ligands with zinc(II) have been carried out by many research groups. Many of these studies have resulted in isolable compounds that have been suitable for crystallographic structural studies. There have been several annual reviews of zinc chemistry [1], and we have recently completed a classification and review of the structures of zinc coordination compounds [2]. This present review covers the structures of organozinc compounds having a Zn–C bond. This field is still growing in importance, as can be concluded from the relatively large number of recent publications.

### 2. Mononuclear organozinc compounds

Structural data for mononuclear organozinc compounds are given in Table 1. The zinc atom can be two or four coordinated. There are four derivatives [3–5] in which the zinc atom is linearly coordinated by C donor ligands with Zn–C bond distances ranging from 1.950(2) to 1.980(4) Å with a mean value of 1.967 Å.

In the remaining 12 derivatives [7–15] the zinc atom is tetrahedrally coordinated. The ligands are unidentate and bidentate, and various degrees of distortion are consequently observed. For the bidentate ligands there are different sizes of the metalloring, causing variations in the bite angles. The effects of both electronic and steric factors can be seen in the variation of the L–Zn–L bond angles. For the five-membered metallocycles, the mean L–Zn–L bond angle is 72.3° for O-donor ligands, 75.0° and 84.5° for unsaturated and saturated N-donor ligands respectively, and 85.7° for a C plus P donor ligand, reflecting the difference in the covalent radius of oxygen (0.73 Å), nitrogen (0.75 Å), carbon (0.77 Å) and phosphorus (1.10 Å).

In the series of unidentate ligands the mean Zn–L distances increase with increasing covalent radius of the coordinated atom in the sequence 1.99 Å (C, 0.77 Å) < 2.26 Å (Cl, 0.99 Å) < 2.64 Å (I, 1.33 Å). In the series of bidentate ligands the mean Zn–L distance increases in the order 2.185 Å (O) < 2.234 Å (N), which reflects the trend of covalent radius of the coordinating atom. The mean Zn–L distance increases with increasing coordination number, as expected, from 1.97 to 1.99 Å for two- and four-coordinated species, respectively.

In  $\text{Zn}(\text{C}_{22}\text{H}_{22}\text{O}_2)(\text{CH}_2\text{I})_2$  [8], two crystallographically independent molecules are present, differing in their degrees of distortion. The coexistence of two or more species, differing only in their degrees of distortion, is typical of the general class of distortion isomerism and occurs often in copper (II) complex chemistry [16]. Most of these species are colourless, as might be expected on electronic grounds.

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Table 1  
Crystallographic and structural data for mononuclear organozinc compounds <sup>a</sup>

Compound (colour)	Crystal class Space group Z	a (Å) b (Å) c (Å)	α (°) β (°) γ (°)	Chromo- phore	Zn–L (Å)		L–Zn–L (°)	Ref.
Zn((2,4- <sup>t</sup> Bu) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> ) <sub>2</sub> (colourless)	m P2 <sub>1</sub> /n 2	9.748(2) 11.444(3) 12.511(3)	110.46(2)	ZnC <sub>2</sub>	C <sup>b</sup>	1.969(8, 0)	C,C 180,0(1)	[3]
Zn((MeOMe <sub>2</sub> Si)(Me <sub>3</sub> Si) <sub>2</sub> C) <sub>2</sub> (not given)	m P2 <sub>1</sub> /n 2	9.283(6) 17.393(7) 10.407(3)	104.88(4)	ZnC <sub>2</sub>	C	1.980(4, 0)	C,C 180	[4]
Zn((HOMe <sub>2</sub> Si)(Me <sub>3</sub> Si) <sub>2</sub> C) <sub>2</sub> (not given)	tr P $\bar{1}$ 2	9.324(2) 11.275(3) 15.708(2)	80.39(2) 85.25(1) 70.95(2)	ZnC <sub>2</sub>	C	1.965(2) 1.970(2)	C,C 175.9(1)	[4]
[Zn(Et) <sub>2</sub> ](18-crown-6) (colourless)	tr P $\bar{1}$ 1	8.503(6) 8.719(8) 8.296(7)	111.8(1) 114.8(1) 97.9(1)	ZnC <sub>2</sub>	C	1.950(2)	C,C 180	[5]
{(C <sub>5</sub> H <sub>8</sub> ) <sub>2</sub> SMe}[Zn((C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> - SCH <sub>2</sub> ) <sub>3</sub> ] (colourless)	m P2 <sub>1</sub> /c 4	15.03(5) 15.19(5) 16.97(5)	116.2	ZnI <sub>3</sub> C	I C	2.64(1, 4) 2.14(3)	I,I 108.7(4, 2.3) I,C 110(1, 10)	[6]
Zn(C <sub>16</sub> H <sub>24</sub> O <sub>5</sub> )(Ph) <sub>2</sub> (colourless)	m P2 <sub>1</sub> /n 8	14.775(3) 18.252(3) 20.082(1)	103.29(1)	ZnO <sub>2</sub> C <sub>2</sub>	O PhC	2.308(3, 85) 1.958(4, 14)	O,O 73.0(9, 4) <sup>c</sup> C,C 147.7(2, 2.2) O,C 102.9(1, 6.1)	[7]
Zn(C <sub>14</sub> H <sub>15</sub> O <sub>4</sub> Br)(Ph) <sub>2</sub> (colourless)	m P2 <sub>1</sub> /n 4	9.000(1) 12.887(1) 19.671(1)	95.66(1)	ZnO <sub>2</sub> C <sub>2</sub>	O PhC	2.269(6, 5) 1.961(8, 2)	O,O 71.6(2) <sup>c</sup> C,C 139.6(3) O,C 106.2(3, 4.6)	[7]
Zn(C <sub>16</sub> H <sub>23</sub> O <sub>5</sub> Br)(Ph) <sub>2</sub> (colourless)	m P2 <sub>1</sub> /n 4	9.368(1) 10.975(1) 27.051(2)	97.48(2)	ZnO <sub>2</sub> C <sub>2</sub>	O PhC	2.284(3, 45) 1.964(4, 3)	O,O 72.4(1) <sup>c</sup> C,C 146.7(2) O,C 103.3(2, 1.3)	[7]
Zn(C <sub>22</sub> H <sub>22</sub> O <sub>2</sub> )(CH <sub>2</sub> I) <sub>2</sub> <sup>d</sup> (not given)	tr P $\bar{1}$ 2	7.367(7) 11.108(4) 11.728(5)	105.42(4) 91.67(3) 94.57(3)	ZnO <sub>2</sub> C <sub>2</sub>	O C	2.15(1, 5) 1.95(2, 3)	O,O 72.7(4) <sup>c</sup> C,C 138.4(7) O,C 106.6(6, 2.9)	[8]
				ZnO <sub>2</sub> C <sub>2</sub>	O C	2.22(1, 2) 2.02(2, 1)	O,O 71.7(4) <sup>c</sup> C,C 137.5(6) O,C 107.1(5, 9)	
Zn( <sup>t</sup> Bu-dab)(Me) <sub>2</sub> (orange)	m P2 <sub>1</sub> /n 4	6.980(1) 20.620(2) 10.054(1)	90.97(1)	ZnN <sub>2</sub> C <sub>2</sub>	N MeC	2.225(7, 0) 2.010(7, 0)	N,N 75.0 <sup>c</sup> C,C 137.3 N,C not given	[9]
Zn((MeNCH <sub>2</sub> ) <sub>3</sub> )(Me) <sub>2</sub> (white)	or Cmcm 4	13.553(2) 7.399(2) 19.736(4)		ZnN <sub>2</sub> C <sub>2</sub>	N MeC	2.410(4, 0) 1.987(6, 0)	N,N 105.6(2) C,C 145.1(2) N,C 100.3(2)	[10]
Zn{2-(Me <sub>3</sub> Si) <sub>2</sub> Cpy} <sub>2</sub> (not given)	m P2 <sub>1</sub> /c 8	24.45(3) 16.56(2) 16.60(1)	107.82(6)	ZnN <sub>2</sub> C <sub>2</sub>	N C	not given 2.049(4, 0)	Not given	[11]
Zn(N <sub>4</sub> Me <sub>4</sub> )(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (not given)	or P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> 4	7.098(1) 15.926(2) 17.924(3)		ZnN <sub>2</sub> C <sub>2</sub>	N C	2.19(2, 4) 1.95(3, 5)	Not given	[12]
Zn((CH <sub>2</sub> ) <sub>3</sub> NMe <sub>2</sub> ) <sub>2</sub> (not given)	or Fdd2 8	17.044(1) 24.734(2) 6.103(1)		ZnN <sub>2</sub> C <sub>2</sub>	N C	2.307(4, 0) 1.984(5, 0)	N,N 109.7(1) C,C 156.4(2) N,C 100.7(1, 7.5)	[13]

Table 1 (continued)

Compound (colour)	Crystal class	<i>a</i> (Å)	$\alpha$ (°)	Chromo- phore	Zn–L		L–Zn–L		Ref.
	Space group	<i>b</i> (Å)	$\beta$ (°)		(Å)		(°)		
	<i>Z</i>	<i>c</i> (Å)	$\gamma$ (°)						
Zn{Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> } <sub>2</sub> (colourless)	<i>m</i>	14.224(6)		ZnC <sub>2</sub> P <sub>2</sub>	C	2.01(1, 1)	C,C	147.1(4)	[14]
	<i>P</i> 2 <sub>1</sub> / <i>a</i>	19.340(9)	102.14(3)		P	2.585(3, 13)	P,P	105.72(9)	
	4	9.984(2)					C,P	85.7(3, 2) <sup>c</sup> 114.5(2, 3.5)	
Zn(Me <sub>4</sub> en)(C <sub>5</sub> H <sub>7</sub> )Cl (colourless)	<i>m</i>	8.435(2)		ZnN <sub>2</sub> CCl	N	2.156(6, 5)	N,N	84.5(3) <sup>c</sup>	[15]
	<i>P</i> 2 <sub>1</sub> / <i>c</i>	13.587(2)	96.50(2)		C	2.030(12)	N,C	119.1(4, 9)	
	4	12.096(2)			Cl	2.263(3)	N,Cl	104.8(2, 3)	
							C,Cl	118.0(4)	

<sup>a</sup> Where more than one chemically distance or angle is present the mean value is tabulated. The first number in parentheses is the estimated standard deviation and the second number is a maximum deviation from the mean value.

<sup>b</sup> The chemical identity of the coordinated atom of the ligand is specified in these columns.

<sup>c</sup> Five-membered metalocyclic ring.

<sup>d</sup> There are two crystallographically independent molecules.

### 3. Binuclear and oligonuclear organozinc compounds

Crystallographic and structural data for binuclear and oligonuclear organozinc compounds are collected in Table 2. There are ten species of binuclear organozinc compounds, with two distinct types of bridging, the distorted edge-shared bitrigonal or bitetrahedral structure with two bridging ligands being the most common. In five derivatives [17–20], two oxygen ligands serve as bridges. In two other species [21,22], two nitrogen ligands also serve as bridges. In two examples the bridges involve two sulphur ligands [19,23].

There is a relationship between the covalent radius of the bridging atom and the Zn–L–Zn angle. The angle closes as the covalent radius of the L donor atom increases. For example, the mean Zn–L–Zn angles and the covalent radii of the bridging atom are; 99.5° and 0.73 Å for O, 85.5° and 0.75 Å for N, and 85.2° and 1.02 Å for S.

The mean Zn–C distances increase with increasing coordination number from 1.950 Å (three coordinated) to 1.996 Å (four coordinated). The mean Zn–L (bridge) distances increase with increasing covalent radius of the coordinated atom and with coordination number in the sequence 1.957 Å (three coordinated) and 2.080 Å (four coordinated) (O, 0.73 Å) < 2.072 Å (N, 0.75 Å) < 2.399 Å (S, 1.02 Å).

The structure of [Zn(<sup>t</sup>BuCH<sub>2</sub>CO<sub>2</sub>)(THF)Br]<sub>2</sub> [24] is shown in Fig. 1. As can be seen, the dimeric unit forms an eight-membered non-planar ring. The zinc atoms are tetrahedrally surrounded by two oxygen, one carbon and one bromine atom (Table 2).

There are three trinuclear derivatives [19]. In two of them [Zn{μ-S(2,4,6-R<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)}(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>3</sub>] (R = isopropyl or tert-butyl), the cores consist of six-membered rings that are comprised of alternating zinc and sulphur atoms. While the (Zn–S)<sub>3</sub> ring in the former has a structure that deviates from strict planarity towards a chair conformation, in the latter the (Zn–S)<sub>3</sub> ring is much closer to planarity. Each zinc has trigonal coordination (Table 2).

The structure of the third trinuclear derivative is shown in Fig. 2. The molecular unit is comprised of an almost linear array of three zinc atoms (Zn–Zn–Zn, 175.7 (1)°) that are bridged by four diisopropylphenoxy groups. Each of the terminal zinc atoms is further coordinated to one alkyl group. The central zinc atom has a distorted tetrahedral geometry whereas the two terminal zinc atoms have a trigonal–planar coordination [19].

Structural data for tetranuclear organo–zinc compounds are summarized in Table 2. In colourless Zn<sub>4</sub>(Et<sub>2</sub>NCO<sub>2</sub>)<sub>6</sub>(Me)<sub>2</sub> [25], the zinc atoms lie in a plane and the unit is centrosymmetric with two independent zinc atoms. Four carbamates bond along the edge of the Zn<sub>4</sub> parallelogram and two further carbamates bridge across the diagonal of the parallelogram above and below the plane of the zinc atoms. The main structural feature of another two derivatives [19,26] is the distorted Zn<sub>4</sub>O<sub>4</sub> cubane core. Both Zn and O possess highly distorted tetrahedral coordination (Table 2).

The structure of colourless [(Et)Zn(Me(<sup>t</sup>Bu)N(H)C=(MeO)CO)]<sub>4</sub> [27] is shown in Fig. 3. The tetrameric associate consists of four crystallographically independent ZnOCCN units which are linked via zinc–oxygen–zinc bridges (average Zn–O–Zn angle of 131.8(3)°) and form a central eight-membered Zn<sub>4</sub>O<sub>4</sub> ring.

In another colourless derivative [28], the structure contains an eight-membered Zn<sub>4</sub>O<sub>4</sub> ring formed by

Table 2  
Crystallographic data for binuclear and oligonuclear organozinc compounds<sup>a</sup>

Compound (colour)	Crystal class	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>α</i> (°)	<i>β</i> (°)	<i>γ</i> (°)	Chromophore	Zn–L (Å)	Zn–L (Å)	Zn–Zn (Å) Zn–L–Zn (°) μL–Zn–μL (°)	L–Zn–L (°)	Reference
[Zn(μ-OH)(C(SiPhMe <sub>2</sub> ) <sub>3</sub> ) <sub>2</sub> ] (not given)	m C2/c 4	25.877(7) 14.596(3) 13.990(4)			94.56(3)			ZnO <sub>2</sub> C	μHO C	1.899(9) 1.953(7)	Not given 102.3(3) 77.5(3)	O,C <sup>b</sup> 138.9(3) 143.5(3)	[17]
[Zn(μ-O(Me)CC(H)N <sup>t</sup> Bu)(Et)] <sub>2</sub> (colourless)	tr P $\bar{1}$ 1	7.57(1) 8.82(2) 11.14(1)	102.6(1) 91.8(1) 114.4(2)					ZnO <sub>2</sub> NC	μO N EtC	2.07(1, 5) 2.21(2) 1.99(2)	95.8(5) 84.2(5)	O,N 114.3(6) 121.3(7, 9.3) 124.9(7)	[18]
[Zn(μ-O(2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ))(C(SiMe <sub>3</sub> ))] <sub>2</sub> (colourless)	or P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> 4	8.797(6) 19.016(17) 22.437(18)						ZnO <sub>2</sub> C	μO C	1.950(10, 25) 1.923(17)	Not given 100.3(4, 5) 79.8(4, 6)	O,C 136.7(6, 5) 143.5(6, 1)	[19]
[Zn(μ-O(2,4,6- <sup>t</sup> BuC <sub>6</sub> H <sub>2</sub> ))(C(SiMe <sub>3</sub> ))] <sub>2</sub> (colourless)	m P2 <sub>1</sub> /a 2	9.344(2) 18.872(4) 13.056(5)	92.38(3)					ZnO <sub>2</sub> C	μO 2.021(4) C	1.958(4) 98.4(2) 1.948(6)	Not given 81.6(2)	O,C 133.8(2) 144.4(2)	[19]
K <sub>2</sub> [Zn(μ-O <sup>t</sup> Bu)(Et)] <sub>2</sub> (colourless)	tr P $\bar{1}$ 1	8.365(2) 8.383(2) 9.316(2)	73.56(2) 105.18(2) 114.51(2)					ZnO <sub>2</sub> C <sub>2</sub>	μO C	2.094(4, 4) 2.056(7, 2)	Not given 100.4(3) 78.56(2)	Not given	[20]
[Zn(μ-MPH) <sub>2</sub> (Me)] <sub>2</sub> (not given)	or P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> 4	7.57(2) 14.95(3) 20.43(4)						ZnN <sub>2</sub> C	μN MeC	2.072(9, 10) 1.948(18, 19)	Not given 89.3(3, 1) 90.7(3, 1)	N,C 134.6(6, 7)	[21]
Zn <sub>2</sub> (C <sub>20</sub> H <sub>28</sub> N <sub>3</sub> )(Et) <sub>2</sub> (colourless)	or Pbca 8	16.98(2) 17.76(1) 17.63(1)						ZnN <sub>3</sub> C	N μN EtC	2.126(6, 4) 2.085(6, 16) 1.978(8, 4)	Not given 82.5(2, 4) 97.5	N,N 74.3(2, 1) <sup>c</sup> 83.6(2, 1) <sup>c</sup> 96.0(2, 0) 129.2(3, 9.8)	[22]
[Zn(μ-SCPh <sub>3</sub> )(C(SiMe <sub>3</sub> ))] <sub>2</sub> (colourless)	tr P $\bar{1}$ 1	9.396(3) 10.609(4) 11.765(4)	113.88(3) 94.15(3) 92.89(3)					ZnS <sub>2</sub> C	μS C	2.399(1, 18) 1.976(4)	Not given 83.2(1) 96.8(1)	S,C 103.5(1) 131.1(1, 4.0)	[19]
[Zn(S <sub>2</sub> CNET) <sub>2</sub> (Me)] <sub>2</sub> (not given)	m P2 <sub>1</sub> /c 2	6.776(1) 10.341(4) 14.479(5)	97.3(3)					ZnS <sub>3</sub> C	S μS MeC	2.370(3) 2.506(4, 6) 1.958(8)	Not given 87.1 92.9(2)	S,μS 74.3(2) <sup>d</sup> 97.2(1) 137.8(3)	[23]
[Zn( <sup>t</sup> BuCH <sub>2</sub> CO <sub>2</sub> )(THF)Br] <sub>2</sub> (not given)	m P2 <sub>1</sub> /n 2	10.322 12.357 11.654	112.65					ZnO <sub>2</sub> CBr	O C THF O Br	2.01 2.03 2.07 2.35	2.01 2.03 2.07 2.35	O,C 121.2(4, 5.6) 111.0	[24]

$[\text{Zn}(\mu\text{-S}(2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2)(\text{Me}_3\text{SiCH}_2)_3(\text{colourless}))]_3$	m $P2_1/c$ 4	18.135(8) 13.035(5) 30.923	96.34(3)	ZnS <sub>2</sub> C	$\mu\text{S}$ C	2.308(2, 19) 1.957(6, 1)	Not given 130.3(1, 1.5)	S,S S,C	103.2(1, 1.6) 121.9(2, 1.2) 134.7(2, 2.0)	[19]
$[\text{Zn}(\mu\text{-S}(2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)(\text{Me}_3\text{SiCH}_2)_3(\text{colourless}))]_3$	tr $P\bar{1}$ 2	10.376(3) 15.543(6) 26.475(7)	103.04(3) 97.35(2) 101.15(1)	ZnS <sub>2</sub> C	$\mu\text{S}$ C	2.329(2, 38) 1.957(7, 9)	Not given 140.6(1, 6.7)	S,S S,C	99.8(1, 4, 3) 119.4(3, 5.6) 140.5(3, 6.5)	[19]
$[\text{Zn}_3(\mu\text{-O}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_4(\text{Me}_3\text{SiCH}_2)_2(\text{colourless}))]_2$	tr $P\bar{1}$ 2	12.229(3) 12.465(3) 22.161(5)	103.97(2) 90.23(2) 106.93(2)	ZnO <sup>2</sup> C (X2) ZnO <sub>4</sub> (X1)	$\mu\text{O}$ C $\mu\text{O}$	1.959(8, 10) 1.941(3, 8) 1.969(2, 16)	Not given 100.1(1, 1)	O,O O,C	80.2(1, 1) 133.2(1, 9) 146.4(1, 7)	[19]
$\text{Zn}_4(\text{Et}_2\text{NCO}_2)_6(\text{Me})_2$	tr $P\bar{1}$ 1	11.747(1) 11.251(2) 10.422(1)	108.43(2) 76.48(2) 72.35(2)	ZnO <sub>3</sub> C (X2) MeC ZnO <sub>5</sub> (X2)	$\mu\text{O}$ O MeC $\mu\text{O}$ O	2.064(6, 69) 1.934(6) 1.945(8) 1.985(6) 2.591(7)	Not given	$\mu\text{O},\text{O}$ $\mu\text{O},\text{C}$ O,C $\mu\text{O},\text{O}$	95.2(3, 3.2) 118.4(3, 8.0) 126.5(3) 56.3(3) <sup>d</sup> 104.5(3, 13.9) 162.5(3) 114.6(3, 7.8)	[25]
$[\text{Zn}(\mu_3\text{-O}(1\text{-ad}))(\text{Me}_3\text{SiCH}_2)_4(\text{colourless}))]_4$	tg $I4_1/a$ 4	21.307(10) – 13.365(8)	–	ZnO <sub>3</sub> C	$\mu_3\text{O}$ C	2.089(2, 41) 1.988(4)	Not given 96.8(1, 1.5)	O,O O,C	82.7(1, 1.2) 122.7(1, 1.4) 143.6(1)	[19]
$[\text{Zn}(\mu_3\text{-OMe})(\text{Me})_4(\text{colourless}))]_4$	or $P2_1\text{-}2_1$ 4	7.481(15) 7.673(15) 29.42(5)	–	ZnO <sub>3</sub> C	$\mu_3\text{O}$ MeC	2.078(15, 39) 1.946(33, 16)	3.086(5, 9) 95.9(7, 1.5)	O,O O,C	83.8(6, 1.1) 129.4(9, 6.3)	[26]
$[(\text{Et})\text{Zn}(\text{Me}^i\text{Bu})(\text{H})\text{C}=(\text{MeO})\text{CO}]_4(\text{colourless}))]_4$	m $P2_1/n$ 4	20.063(1) 12.875(1) 20.414(1)	101.72(1)	ZnO <sub>2</sub> NC	$\mu\text{O}$ N EtC	2.049(6, 27) 2.211(8, 20) 1.978(9, 5)	Not given 131.8(3, 7)	O,O O,N	95.3(2, 6) 81.9(3, 2) <sup>c</sup> 99.8(3, 1.3) 119.5(3, 4.9) 129.4(4, 9)	[27]
$[\text{Zn}_2(\mu_3\text{-OPh})(\text{dimh})(\text{Ph})]_2(\text{colourless}))]_2$	m $P2_1/c$ 2	12.90(1) 11.92(1) 23.21(1)	125.10(5)	ZnO <sub>3</sub> C (X2)	$\mu_3\text{O}$ $\mu\text{O}$ PhC	2.04(1) 2.05(1, 1) 1.97(2)	Not given 96.9(6, 1.2) 101.7(6, 1.1)	O,O O,C	82.0(5, 5) 94.9(6) 119.3(7) 131.2(9, 2) 78.7 170.1(2)	[28]
$[\text{Zn}(\text{Me}_3\text{CS})(\text{Me})_5(\text{colourless}))]_5$	m $P2_1/c$ 4	9.59(2) 39.04(6) 12.13(2)	117.13(17)	ZnS <sub>3</sub> C	$\mu_4\text{S}$ 2.712(8) 2.982(8) $\mu_3\text{S}$ $\mu\text{S}$ MeC	2.514(8) 77.6(3, 4.8) 91.4(3, 3.7) 2.439(9, 3.6) 2.297(9, 2.5) 2.01(4, 9)	3.387–4.996(6)	S,S S,C	78.4(3, 2.1) 91.7(3, 7.3) 111.5(8, 5) 128.9(3, 3.2) 126.4(12, 9.1)	[29]

Table 2 (continued)

Compound (colour)	Crystal class			Chromophore	Zn–L (Å)	Zn–Zn (Å) Zn–L–Zn (°) $\mu$ L–Zn– $\mu$ L (°)	L–Zn–L (°)	Reference
	Space group	$a$ (Å)	$\alpha$ (°)					
$Zn_7(\text{MeO})_8(\text{Me})_6$ (not given)	<i>tr</i>	10.08	115.4	$ZnO_6$ (X1)	$\mu_3O$	2.073(15, 5) 2.170(17)	O,O	93–98 [30]
	$P\bar{1}$	8.76	117.3					
	1	10.61	92.1	$ZnO_3C$ (X6)	$\mu_3O$ MeC	2.069(17, 78) 1.953		
$Zn(\text{MeO})_8(\text{Et})_6$ (colourless)	<i>m</i>	11.276(3)	106.68(2)	$ZnO_6$ (X1)	$\mu_3$	2.06 2.13(3)	O,O	80.2 [31]
	$P2_1/c$	15.741(3)						
	2	10.715(2)		$ZnO_3C$ (X6)	$\mu_3O$ EtC	2.18(3) 2.06 2.07	O,O 82.5	
$\{Zn(C_5H_5)Me\}_n$ (colourless)	or	8.944(2)	?	$ZnC_4$	MeC ( $C_5H_5$ )	1.96(1, 1) 2.22–2.81	Not given	[32]
	<i>Cmcm</i>	7.044(2)						
	?	9.476(2)						

<sup>a</sup> Where more than one chemically equivalent distance or angle is present the mean value is tabulated. The first number in parentheses is the estimated standard deviation and the second number is a maximum deviation from the mean value.

<sup>b</sup> The chemical identity of the coordinated atom of the ligand is specified in these columns.

<sup>c</sup> Five-membered metallocyclic ring.

<sup>d</sup> Four-membered metallocyclic ring.

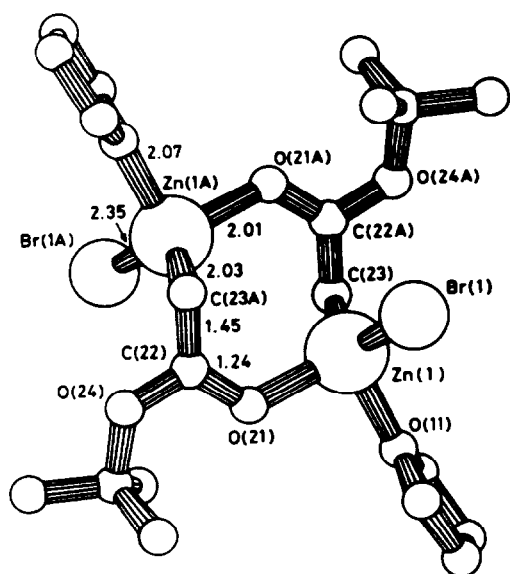


Fig. 1. Crystal structure of  $[\text{Zn}(\text{}^t\text{BuCH}_2\text{CO}_2)(\text{THF})\text{Br}]_2$  [24].

alternating zinc and oxygen atoms. This ring is bridged twice by the oxygen atoms of the two  $\text{PhZnOPh}$  moieties (Table 2).

Colourless  $[\text{Zn}(\text{Me}_3\text{CS})(\text{Me})_5]$  [29] exists in the crystal as discrete pentamers. This is the only such example in the series of organozinc compounds. The zinc atoms lie near the corners of a square-based pyramid with the apical atom  $\text{Zn}(5)$  closer to  $\text{Zn}(3)$  and  $\text{Zn}(4)$  than to  $\text{Zn}(1)$  and  $\text{Zn}(2)$  (Fig. 4, and Table 2).

The molecular structure of  $\text{Zn}_7(\text{MeO})_8(\text{Me})_6$  [30] is shown in Fig. 5. The centrosymmetric complex consists of two enantiomorphous distorted cubes which share a corner, the centre of symmetry. The zinc atoms occupy the corners of a tetrahedron, and the oxygen atoms occupy the corners of an interpenetrating but smaller

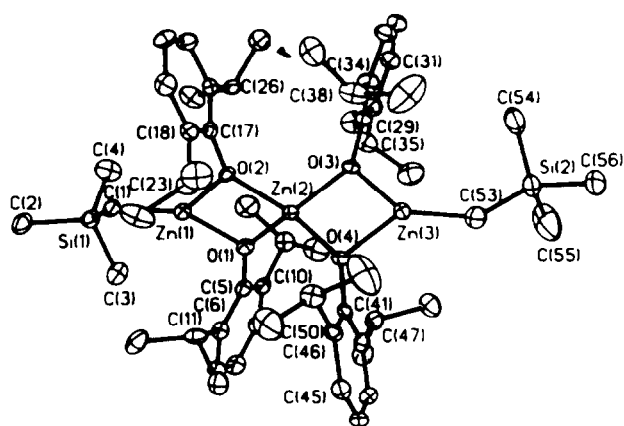


Fig. 2. Crystal structure of  $[\text{Zn}_3\{\mu\text{-O}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}_4(\text{Me}_3\text{SiCH}_2)_2]$  [19].

tetrahedron. This familiar structure is present in colourless  $\text{Zn}_7(\text{NCO})_8(\text{Et})_6$  [31] (Table 2).

Colourless  $[\text{Zn}(\text{C}_5\text{H}_5)(\text{Me})_n]$ , adopts a puckered  $-\text{Zn}(\text{C}_5\text{H}_5)\text{Zn}(\text{C}_5\text{H}_5)\text{Zn}(\text{C}_5\text{H}_5)-$  chain structure in which the bridging cyclopentadienyl groups coordinate in a di or trihepto manner to the bridged zinc atoms, apparently functioning as five-electron ligands [32]. The methyl–zinc distance is 1.96 Å. Each zinc atom is thus surrounded by a distorted trigonal arrangement of three ligands. Colourless species are by far the more prevalent.

#### 4. Conclusions

Almost 40 organozinc compounds are surveyed in this review. The zinc(II) atoms in the series of mononuclear compounds are found in digonal [3–5] and tetrahe-

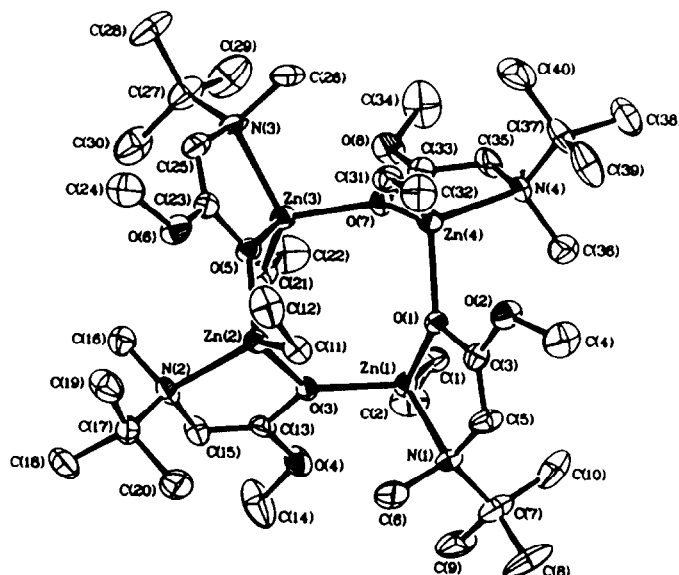


Fig. 3. Crystal structure of  $[(\text{Et})\text{Zn}\{\text{Me}(\text{}^t\text{Bu})\text{N}(\text{H})\text{C}(\text{=MeO})\text{CO}\}]_4$  [27].

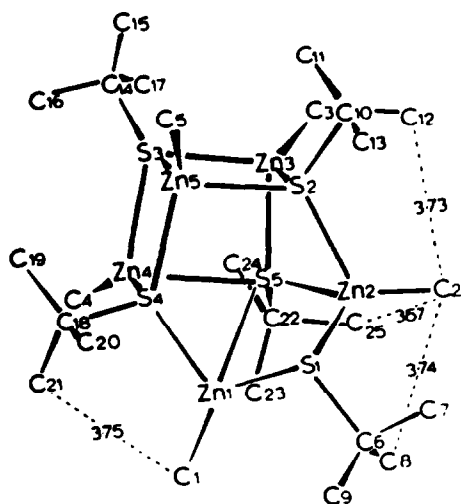


Fig. 4. Crystal structure of  $[\text{Zn}(\text{Me}_3\text{CS})(\text{Me})_5]$  [29].

dral [6–15] environments. There are examples of binuclear [17–24], trinuclear [19], tetranuclear [19,25–28], pentanuclear [29], heptanuclear [30,31] and polynuclear [32] derivatives.

There is the example  $\text{Zn}(\text{C}_{22}\text{H}_{22}\text{O}_2)(\text{CH}_2\text{I})_2$  [8] which contains two crystallographically independent molecules, differing in degree of distortion.

There is a trend for the Zn–L distance to increase with increasing covalent radius of the coordinated atom and also with increasing coordination number.

This review, together with its precursor [2], represents the first overview of crystallographic and structural data for zinc. It is hoped that this review will serve to bring together the overall picture and to stimulate areas of particular interest.

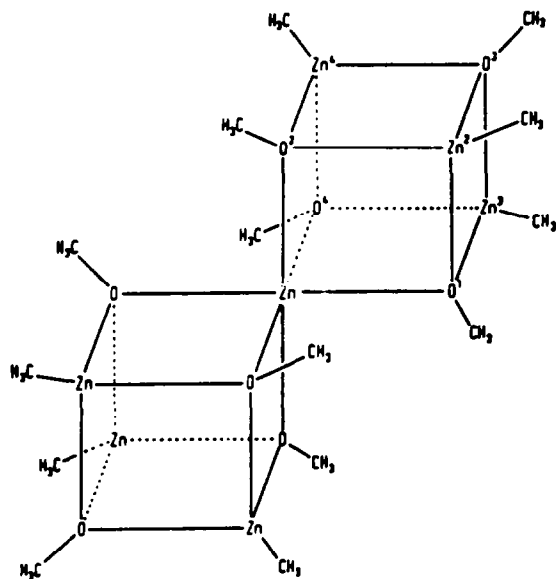


Fig. 5. Crystal structure of  $\text{Zn}_7(\text{MeO})_8(\text{Me})_6$  [30].

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## Appendix A: Nomenclature

<sup>t</sup> Bu	tertiary butyl
<sup>t</sup> Bu-dab	<i>N,N</i> -di-tert-butyl-1,4-diazabutadiene
$\text{C}_5\text{H}_5$	cyclopentadienyl
$\text{C}_5\text{H}_7$	2,4-pentadienyl
$(\text{C}_5\text{H}_9)_2\text{SMe}$	methyl dineopentylsulphonium
$\text{C}_6\text{F}_5$	pentafluorophenyl
$\text{C}_{14}\text{H}_{15}\text{O}_4\text{Br}$	2-bromo-1,3-xylyl-15-crown-4
$\text{C}_{16}\text{H}_{23}\text{O}_5\text{Br}$	2-bromo-1,3-xylyl-18-crown-5
$\text{C}_{16}\text{H}_{24}\text{O}_5$	1,3-xylyl-18-crown-5
$\text{C}_{20}\text{H}_{28}\text{N}_1$	1,2-bis(tert-butylamino)-112-di(2-pyridyl)ethane
$\text{C}_{22}\text{H}_{22}\text{O}_2$	“Wittig–Furukawa” cyclopropanation reagent
dmh	2,2-dimethyl-1,3-hexanedionate
Et	ethyl
m	monoclinic
Me	methyl
or	orthorhombic
py	pyridine
Ph	phenyl
tg	tetragonal
tr	triclinic
THF	tetrahydrofuran

## References

- [1] M.N. Hughes, *Coord. Chem. Rev.*, 37(1981)297; 45(1982)329; 52(1983)1; 58(1984)1; D. Dakternieks, *Coord. Chem. Rev.*, 62(1985)1; 78(1987)125 and 98(1989)279.
- [2] M. Melnik, K. Györyová, J. Skoršepa and C.E. Holloway, to be published.
- [3] R.D. Ernst, J.W. Freeman, P.N. Swepston and D.R. Wilson, *J. Organomet. Chem.*, 402(1991)17.
- [4] F.I. Aigbirhio, S.S. Al-Juaid, C. Eaborn, A. Habtermariam, P.B. Hitchcock and J.D. Smith, *J. Organomet. Chem.*, 405(1991)149.
- [5] A.D. Pajerski, G.L. Berg Stresser, M. Parvez and H.G. Richey, Jr., *J. Am. Chem. Soc.*, 110(1988)4844.
- [6] B.T. Killbourn and D. Felix, *J. Chem. Soc. A*, (1969)163.
- [7] P.R. Markles, G. Schat, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets and A.L. Spek, *Organometallics*, 10(1991)3538.
- [8] S.E. Denmark, J.P. Edwards and S.R. Wilson, *J. Am. Chem. Soc.*, 113(1991)723.
- [9] M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. van Koten, E. Wissing, W.J.J. Smeets and A.L. Spek, *J. Am. Chem. Soc.*, 113(1991)5606.
- [10] M.B. Hursthouse, M. Motevalli, P. O’Brein, J.R. Walsh and A.C. Jones, *Organometallics*, 10(1991)3196.



- [11] M.J. Henderson, R.I. Papasergio, C.L. Raston, A.L. White and M.F. Lappert, *J. Chem. Soc., Chem. Commun.*, (1986)672.
- [12] V.W. Day, D.H. Campbell and C.J. Michejda, *J. Chem. Soc., Chem. Commun.*, (1975)118.
- [13] J. Dekker, J. Boersma, L. Fernholt, A. Haaland and A.L. Spek, *Organometallics*, 6(1987)1202.
- [14] J. Dekker, J.W. Munninghoff, J. Boersma and A.L. Spek, *Organometallics*, 6(1987)1236.
- [15] H. Yasuda, Y. Ohnuma, A. Nakamura, Y. Kai, N. Yasuoka, and N. Kasai, *Bull. Chem. Soc. Jpn.*, 53(1980)1101.
- [16] M. Melnik, *Coord. Chem. Rev.*, 47(1982)239.
- [17] S.S. Al-Juaid, N.H. Buttrus, C. Eaborn, P.B. Hitchcock, A.T.L. Roberts, J.D. Smith and A.C. Sullivan, *J. Chem. Soc., Chem. Commun.*, (1986)908.
- [18] M.R.P. van Viliet, G. van Koten, P. Buysingh, J.T.B.H. Jastrzebski and A.L. Spek, *Organometallics*, 6(1987)537.
- [19] M.M. Olmstead, P.P. Power and S.C. Shoner, *J. Am. Chem. Soc.*, 113(1991)3379.
- [20] R.M. Fabicon, M. Parvez and H.G. Richey, Jr., *J. Am. Chem. Soc.*, 113(1991)1412.
- [21] N.A. Bell, H.M.M. Shearer and C.B. Spencez, *Acta Crystallogr., Sect. C.*, 39(1983)1182.
- [22] A.L. Spek, J.T.B.H. Jastrzebski and G. van Koten, *Acta Crystallogr., Sect. C*, 43(1987)2006.
- [23] M.B. Hursthouse, M.A. Malik, M. Motevalli and P. O'Brien, *Organometallics*, 10(1991)730.
- [24] J. Dekker, J. Boersma and G.J.M. van der Kerk, *J. Chem. Soc., Chem. Commun.*, (1983)553.
- [25] M.B. Hursthouse, M.A. Malik, M. Motevalli and P. O'Brien, *J. Chem. Soc., Chem. Commun.*, (1991)1690.
- [26] H.M.M. Shearer and C.B. Spencez, *Acta Crystallogr., Sect. B*, 36(1980)2046.
- [27] F.M. van der Steen, J. Boersma, A.L. Spek and G. van Koten, *Organometallics*, 10(1991)2467.
- [28] J. Boersma, A.L. Spek and J.G. Noltes, *J. Organomet. Chem.*, 81(1974)7.
- [29] G.W. Adamson, N.A. Bell and H.M.M. Shearer, *Acta Crystallogr., Sect. B*, 38(1982)462.
- [30] M.L. Ziegler and J. Weiss, *Angew. Chem.*, 82(1970)931.
- [31] M. Ishimori, T. Hagiwara, T. Tsuruta, Y. Kai, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Jpn.*, 49(1976)1165.
- [32] T. Aoyagi, H.M.M. Shearer, K. Wade and G. Whitehead, *J. Organomet. Chem.*, 146(1978)C29.