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Slow atmospheric oxidation of diphenylzinc: di-μ-phenoxido-bis[(diethyl ether)phenylzinc(II)]

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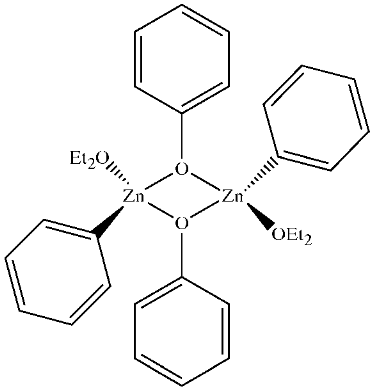
The title compound, $[Zn_2(C_6H_5)_2(C_6H_5O)_2(C_4H_{10}O)_2]$, was isolated from a solution of diphenylzinc in diethyl ether that had been exposed to air. The molecules are dinuclear, with a distorted tetrahedral coordination geometry around the Zn atoms and with molecules situated about a crystallographic inversion centre. Molecules associate *via* three sets of C—H$\cdots\pi$(arene) interactions, leading to a network structure.

Comment

Organozinc reagents are known to be highly sensitive towards atmospheric O_2, as noted by Edward Frankland during his pioneering work on organozinc compounds (see, for example, Frankland, 1852, 1855; Seyferth, 2001). This forced Frankland to develop several ingenious apparatuses in order to synthesize, purify and analyse the highly reactive compounds he had discovered (Frankland, 1855). Low molecular weight dialkylzinc compounds ($ZnMe_2$, $ZnEt_2$ and $ZnPr_2$) ignite spontaneously when exposed to air (Boersma, 1982*a*). Slow oxidation of organozinc reagents by low concentrations of O_2 is known to give rise to the corresponding alkoxides, with zinc organoperoxides as intermediates (Boersma, 1982*b*). The formation of alkoxides by the action of O_2 on dialkylzinc compounds was first reported in the case of diethylzinc by Frankland (1855), who identified zinc ethoxide as one of the products obtained in the reaction of diethyl zinc and O_2.

The title compound, (I), was isolated from a diethyl ether solution of diphenylzinc (standing in a Schlenk tube) after a period of 3.5 years, during which the solution had partially attacked the silicon grease on the stopcock, causing a minute leak of atmospheric O_2 into the tube. Compound (I) is a dinuclear zinc complex, situated about a crystallographic inversion centre (Fig. 1). The coordination geometry around Zn1 is highly distorted tetrahedral, with a Zn1—C1 distance of 1.964 (2) Å, Zn—O bond lengths of 1.9898 (14), 2.0008 (14) and 2.0939 (15) Å, and angles about the Zn centre ranging from 79.31 (6) to 130.39 (7)°. The coordination of diethyl ether to zinc is, perhaps surprisingly, rare among the structures in the Cambridge Structural Database (CSD; Version 5.28 of November 2006; Allen 2002). Only 11 structures were found containing a Zn–OEt_2 fragment. Among these, two examples of organozinc complexes, bis[(μ_2-chloro)(1,1-dichloro-2,2,2-trifluoromethyl)(diethyl ether)zinc(II)] (Behm *et al.*, 1993) and tris(diethyl ether)(ethyl)zinc(II) tetrakis(pentafluorophenyl)borate (Walker *et al.*, 2001), as well as one example of a zinc aryloxide, bis[(diethyl ether)(2,6-diphenylphenoxy)]-zinc(II) (Darensbourg *et al.*, 1999), are found.



(I)

Several crystal structures for zinc aryloxides and organozinc aryloxides have been published and are reported in the CSD, but none of the structures are closely related to (I). 146 structures are found to contain two Zn atoms bridged by two aryloxide groups. Most of these structures include complex aryloxide groups, having, for example, *N*-donor substituents coordinating to Zn, *e.g.* bis{[μ_2-2-(diethylaminomethyl)phenoxo](ethyl)zinc(II)} (Hunger *et al.*, 2005). Structures having a monodentate neutral ligand at Zn, as for (I), are rare. There is

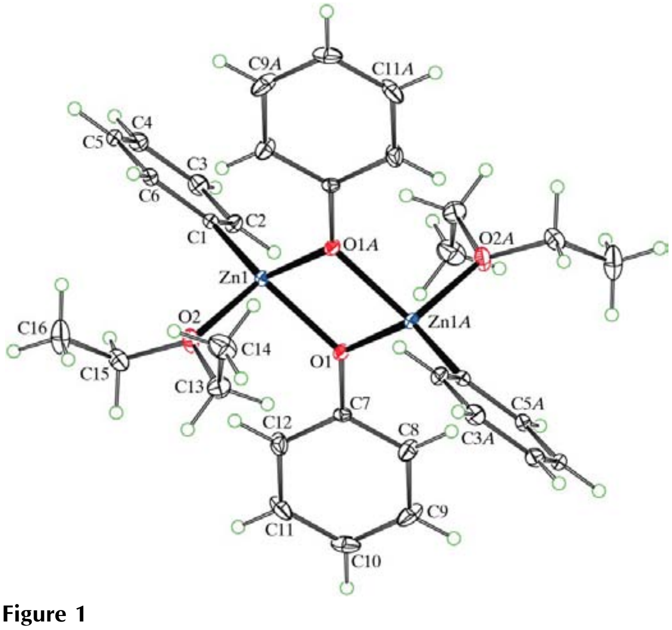


Figure 1
A view of (I), showing the atomic numbering scheme; atoms labelled with the suffix *A* indicate symmetry-related equivalents. Displacement ellipsoids are drawn at the 30% probability level and H atoms are included with radii of an arbitrary size. [Symmetry code: (*A*) $-x+1, -y+1, -z$.]

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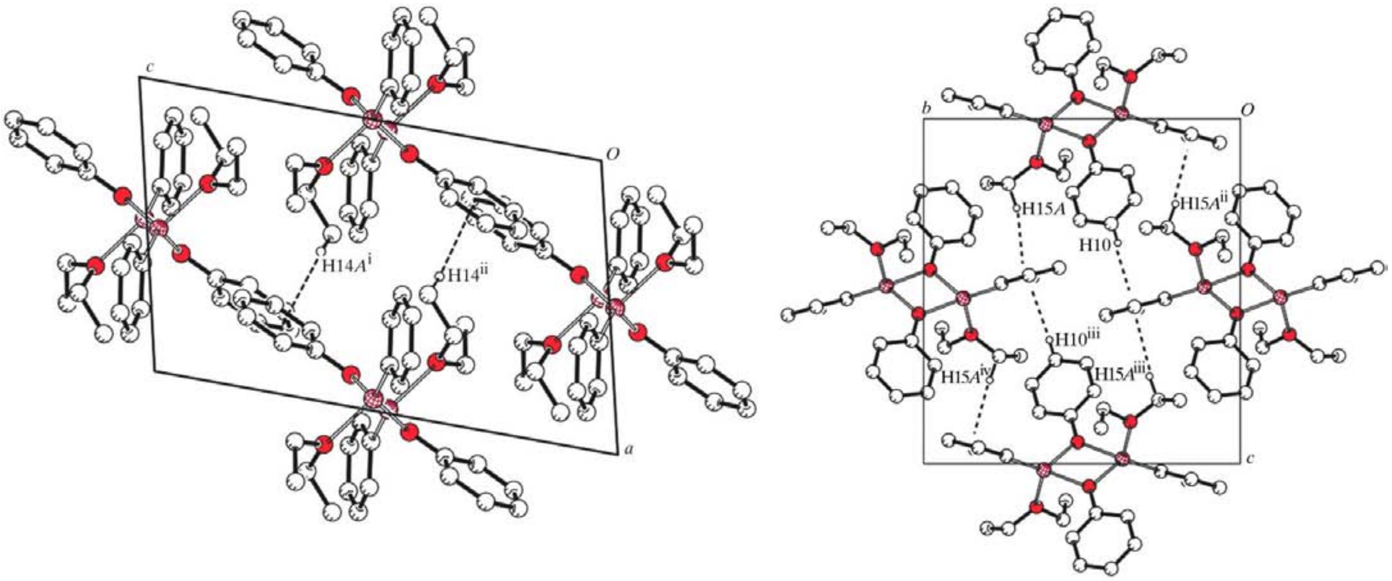
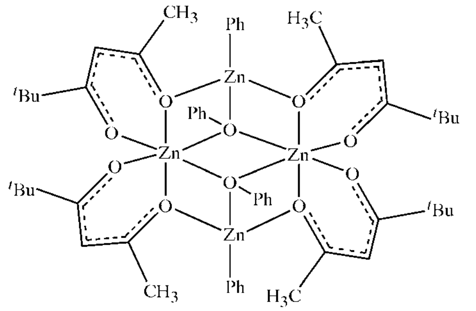


Figure 2

The structure of (I) has three sets of C—H$\cdots\pi$(arene) interactions. The unit cell of (I) is shown as viewed along the *b* axis (left, with the H14*A* interaction) and along the *c* axis (right, with the H10 and H15*A* interactions). [Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.]

only one example of an organozinc aryloxide bearing a coordinating ligand at Zn, *viz.* bis[(μ_2-2,6-dimethylphenoxo)(ethyl)(pyridyl)zinc(II)] (Boyle *et al.*, 2004). Two structures of bridged zinc aryloxides having monodentate neutral ligands at Zn are reported in the CSD, *viz.* bis[(μ_2-2,6-difluorophenoxo)(2,6-difluorophenoxo)(tetrahydrofuran)zinc(II)] and bis[(μ_2-2,6-difluorophenoxo)(2,6-difluorophenoxo)(tricyclohexylphosphine)zinc(II)] tetrahydrofuran solvate (Darensbourg *et al.*, 2000). Another structure somewhat similar to (I) is bis[(μ_2-2,3-dihydro-2,2-dimethylbenzofuranoxide)(chloro)(pyridine)zinc(II)] (Sobota *et al.*, 2000). In addition, there are a number of complexes with three-coordinate Zn atoms. In this category, there is one example of a base-free zinc aryloxide, *viz.* bis[(μ_2-2,6-di-*tert*-butylphenoxo)(2,6-di-*tert*-butylphenoxo)zinc(II)] *n*-pentane solvate (Kunert *et al.*, 2000). Other examples include bis[(μ_2-2,6-di-*tert*-butylphenoxo)(ethyl)zinc(II)] (Parvez *et al.*, 1992) and [(μ_2-2,6-diisopropylphenoxo)(trimethylsilylmethyl)zinc(II)] (Olmstead *et al.*, 1991). There are no structures of Zn(OPh)$_2$ complexes in the CSD, but there are eight structures of derivatives bearing one phenoxide ligand at zinc, *e.g.* bis(μ_2-phenoxo)[*N*-isopropyl-2-(isopropylamino)troponiminato]zinc(II) (Herrmann *et al.*, 2004) and bis(μ_3-phenoxo)tetrakis(μ_2-2,2-dimethyl-3,5-hexanedionato)diphenyltetrazinc(II), (II) (Boersma *et al.*, 1974). Compound (II) is the only example in the CSD of a phenylzinc–phenoxide complex. The Zn$\cdots$Zn distances in this structure are 3.177, 3.239 and 3.171 Å, slightly longer than that in (I) [3.0724 (6) Å].



(II)

The crystal structure of (I) displays three sets of C—H$\cdots\pi$ interactions (Nishio, 2004; Cantrill *et al.*, 2000; Braga *et al.*, 1998; Viswamitra *et al.*, 1993) (Table 1). The shortest set involves atom H14*A* and the (C1–C6)$^{\rm ii}$ phenyl ring [symmetry code: (ii) $x+1, y, z$] and gives rise to chains extending along the *a* axis. The second shortest set of C—H$\cdots\pi$ contacts involves atom H10 and the (C1–C6)$^{\rm i}$ phenyl ring [symmetry code: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$]. These interactions result in layers extending parallel to the (202) set of planes. A third set of interactions can be identified, *viz.* atom H15*A* interacts with the (C1–C6)$^{\rm iii}$ phenyl ring [symmetry code: (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$]. These interactions give rise to layers parallel to $(20\bar{2})$. The three sets of interactions result in a network structure, and these interactions are depicted in Fig. 2.

Zinc aryloxides have found use in carbon dioxide activation and may have future potential as an activator of this greenhouse gas. Darensbourg and co-workers reported that zinc aryloxides catalyse the copolymerization of carbon dioxide and epoxides (Darensbourg & Holtcamp, 1995; Darensbourg *et al.*, 1999). Fixation of carbon dioxide by carboxylation of acetophenone using zinc aryloxide catalysts has also been reported (Kunert *et al.*, 2000).

Experimental

Bromobenzene (4.1 ml, 0.039 mol) was added to a stirred mixture of Mg (1.1 g, 0.045 mol) and diethyl ether (40 ml). The mixture was stirred overnight at ambient temperature. The solution was added dropwise to a suspension of ZnCl$_2$ (2.6 g, 0.019 mol) in diethyl ether

(10 ml) at 273 K. The reaction mixture was stirred at ambient temperature overnight, evaporated and sublimated at 10^{-2} mbar. The white product was dissolved in diethyl ether (4 ml). After 3.5 years of storage at 238 K, the silicon grease had been heavily attacked by the $ZnPh_2$ solution, resulting in leakage of atmospheric O_2 into the Schlenk tube. Large colourless hexagonal prismatic crystals of (I) were isolated.

Crystal data

$[Zn_2(C_6H_5)_2(C_6H_5O)_2(C_4H_{10}O)_2]$
M_r = 619.42
Monoclinic, $P2_1/n$
a = 8.5115 (13) Å
b = 12.8018 (18) Å
c = 14.128 (2) Å
β = 99.814 (5)°
V = 1516.9 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.61 mm^{-1}
T = 100 (2) K
0.30 × 0.25 × 0.15 mm

Data collection

Rigaku R-AXIS-IIC image-plate system diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
T_{min} = 0.559, T_{max} = 0.785
9541 measured reflections
2729 independent reflections
2540 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.080
S = 1.08
2729 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.88 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C1–C6 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10···$Cg1^{i}$	0.93	2.76	3.542 (3)	143
C14—H14A···$Cg1^{ii}$	0.96	2.68	3.539 (3)	149
C15—H15A···$Cg1^{iii}$	0.97	2.88	3.834 (3)	167

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x+1, y, z$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

All H atoms were included in calculated positions (C—H = 0.93–0.97 Å) and refined using a riding model, with U_{iso}(H) values of 1.2 or 1.5 times U_{eq}(C).

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3123). Services for accessing these data are described at the back of the journal.

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