

A μ_4 -oxide-containing a dimeric variant of a sodium dialkyl(amido)-zincate reagent

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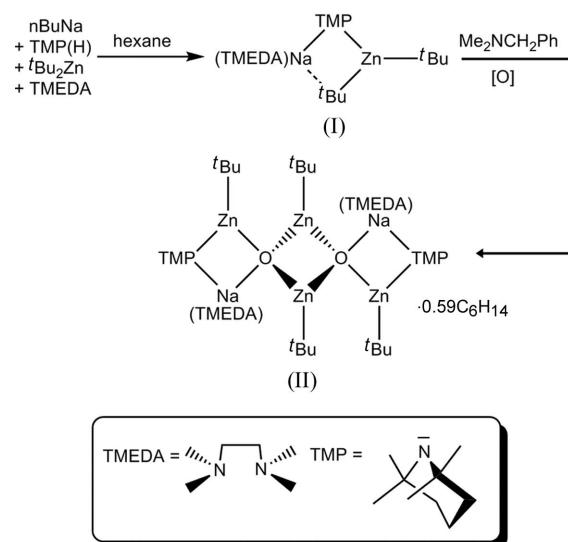
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Post-metallation derivatives of the sodium dialkyl(amido)-zincate reagent (TMEDA)Na(μ -TMP)Zn(*t*Bu)₂ (TMEDA is *N,N,N',N'*-tetramethylethylenediamine and TMP is 2,2,6,6-tetramethylpiperidide) have been of structural interest due to the insight they give into aromatic metallation mechanisms. Here, the aromatic substrate is formally replaced with [ZnO]₂ to give tetra-*tert*-butyldi- μ_4 -oxido-bis(tetramethylethylenediamine- κ^2N,N')bis(μ_2 -2,2,6,6-tetramethylpiperidin-1-ido- $\kappa^2N:N$)-disodiumtetrazinc hexane 0.59-solvate, [Na₂Zn₄(C₄H₉)₄(C₉H₁₈N)₂O₂(C₆H₁₆N₂)₂] \cdot 0.59C₆H₁₄. The crystallographically centrosymmetric complex retains many of the structural features of its parent monomer but has an unusual dimeric structure, with a central planar Zn–O–Zn–O ring joined to two orthogonal near-planar Zn–O–Na–N rings through the distorted tetrahedral geometries of the oxide ions.

Comment

Deprotocination (transformation of a C–H bond to a C–Zn bond) is currently receiving widespread attention from synthetic chemists (*e.g.* Armstrong *et al.*, 2010; Dayaker *et al.*, 2010; Mosrin *et al.*, 2009; Mulvey, 2009) as an improved alternative to lithiation (Snieckus, 1990) for labilizing aromatic substrates towards subsequent regioselective functionalization. A key factor in the development of this new type of metallation has been a series of X-ray crystallographic studies (Mulvey, 2006) that have elucidated the structures of both the zincate reagents and the zincated aromatic intermediates they generate on reaction with aromatic substrates. Germane to the present study, the most studied zincate reagent to date has been the sodium dialkyl(amido)zincate (TMEDA)Na(μ -TMP)Zn(*t*Bu)₂, (I), (TMEDA is *N,N,N',N'*-tetramethylethylenediamine and TMP is 2,2,6,6-tetramethylpiperidide), which adopts a dinuclear contact ion-pair structure (Andrikopoulos *et al.*, 2005) where a trigonal-planar Zn centre is connected to a TMEDA-chelated Na centre through

a bridging TMP ligand (see scheme). Generally, this monomeric dinuclear motif is retained on reaction of this zincate base with aromatic substrates, with the deprotonated fragment replacing one of the alkyl units attached to Zn in a bridging position between the two metal centres (Armstrong *et al.*, 2009). Emphasizing the experimental care that must be taken when performing these acutely air- and moisture-sensitive zincation reactions, in the course of investigating the deprotonating action of (I) towards *N,N*-dimethylbenzylamine we have fortuitously prepared the oxide-containing disodium tetrazinc monoalkyl monoamide complex, [(TMEDA)Na(μ -TMP)Zn₂(μ_4 -O)(*t*Bu)]₂, (II). Whether the oxide derives from moisture or oxygen contamination is not known. Such mixed *s*-block metal–zinc complexes have recently been shown to be important in the production of mixed metal oxide semiconducting nanoparticles (Heitz *et al.*, 2011). By elucidating the crystal structure of the partial hexane solvate of (II), we show that the formal incorporation of zinc oxide (ZnO) into the structure of the starting zincate base leads to a dimerized variant of the structure common to both (I) and its aromatic-containing derivatives.



The molecular structure of (II) (Fig. 1) has a crystallographically imposed centre of symmetry and a highly unusual framework involving three linked four-membered rings. A search of the Cambridge Structural Database (*ConQuest* Version 1.13; Allen, 2002) found only one similar heterometallic structural motif with O and N donors, that of a lithium–indium species (Nöth & Seifert, 2002). Literature examples of heterometallic alkali metal–zinc compounds do not show the same coordination framework. Indeed, they are not normally isolated as 2:4 *M*–Zn species as seen here. Instead, 1:1, 1:2 and 2:2 *M*–Zn species are common [for examples, see (I) and Zhu *et al.*, 2006; Clegg *et al.*, 2009; Baggio *et al.*, 1997; Purdy & George, 1994]. The large organic substituents ensure that the discrete units of (II) interact with each other only *via* hydrophobic interactions. The packing could formally be described as stacking of the central Zn–O–Zn–O rings along the *c* direction, but as the distance between the rings is that of the *c*-cell dimension [12.7375 (6) Å] this is far

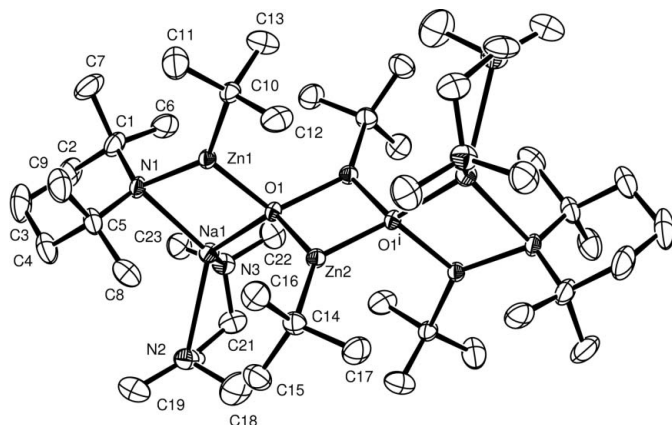


Figure 1
The molecular structure of (II), showing 50% probability displacement ellipsoids. H atoms and the partial hexane solvent molecule have been omitted for clarity. [Symmetry code: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z$.]

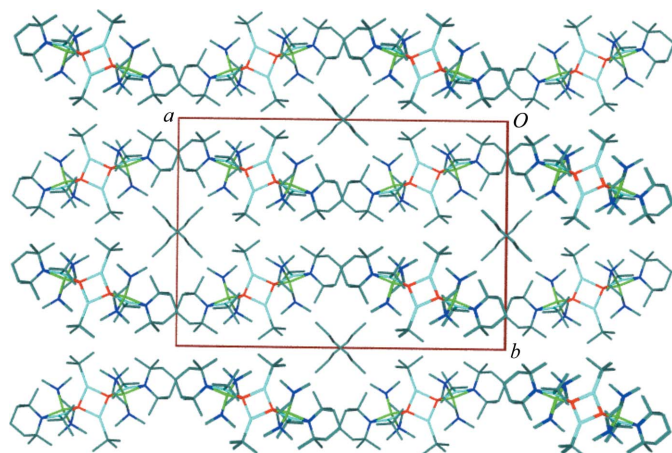


Figure 2
A packing diagram for (II), viewed along the *c* direction.

from a real intermolecular interaction. The hexane solvent molecules lie in channels that run parallel to the *c* axis (Fig. 2).

Within the context of previous work on similar metal-alkyl organometallics, the oxide ions of (II) are also unusual. This is partly because aerobic contamination of such systems typically results in the creation of alkoxide ligands and hence alkoxide complexes (Conway *et al.*, 2005), and this only where complete decomposition of all organometallic species is avoided. Where oxide has been incorporated into similar main group metal amides, it is normally observed to lie at the centre of inverse-crown ether complexes in a square-planar geometry (see, for example, Forbes *et al.*, 2000). However, in (II), the oxide ion is four-coordinate but is much nearer to tetrahedral than to square-planar geometry [angular range = 88.36 (6)–125.94 (7)°]. This geometry about oxygen ensures that the central, strictly planar, Zn–O–Zn–O ring plane is perpendicular to the two Zn–O–Na–N ring planes. [The dihedral angle between the ring planes is 89.57 (3)°. The Zn–O–Na–N ring deviates slightly from planarity, with the metal atoms displaced ‘down’ and the ligand atoms ‘up’. The maximum deviation from the plane is -0.0414 (7) Å for atom Zn1.]

The outer Zn–O–Na–N rings and their substituents retain many of the structural features seen in the Zn–C–Na–N-based rings of aromatic derivatives of (I). Thus, Table 1 shows that each of the crystallographically independent Zn centres of (II) has a three-coordinate geometry, with distortions away from trigonal-planar geometry due to the constraints of being part of the Zn–O–Zn–O and Zn–O–Na–N four-membered rings. Note that both the Zn–O and Zn–C distances for atom Zn2 with its OOC coordination are slightly shorter than the comparable bond distances involving atom Zn1 with its ONC coordination mode. The Na centres are four-coordinate and have an ONNN coordination shell. The three unique Na–N bonds display considerable variation in length, with the bond to the anionic TMP ligand understandably shorter than the two bonds involving neutral TMEDA, despite the bridging nature of the TMP ligand.

Experimental

Under what were assumed to be stringently air- and moisture-free conditions and in a Schlenk tube under argon, ⁿBuNa (2 mmol, 0.16 g) was suspended in hexane (10 ml) and sonicated for 10 min to form a fine dispersion. TMP(H) (2 mmol, 0.34 ml) was introduced and the subsequent yellow suspension was stirred for 1 h. In a separate Schlenk tube, ^tBu₂Zn (2 mmol, 0.36 g) was dissolved in hexane (10 ml) and transferred to the already prepared NaTMP *via* a cannula. TMEDA was then added (2 mmol, 0.3 ml) and the resulting suspension was gently heated to produce a homogeneous yellow solution. *N,N*-Dimethylbenzylamine (2 mmol, 0.3 ml) was added and the reaction mixture was stirred overnight. The resulting orange solution was concentrated by removal of the solvent *in vacuo* and was transferred to a refrigerator (at 278 K). A small number of colourless crystals of (II) were deposited overnight. The synthesis has not been reproduced.

Crystal data

[Na ₂ Zn ₄ (C ₄ H ₉) ₄ (C ₉ H ₁₈ N) ₂ O ₂ · (C ₆ H ₁₆ N ₂) ₂ ·0.59C ₆ H ₁₄	$\beta = 97.565$ (4)°
$M_r = 1131.65$	$V = 6479.5$ (5) Å ³
Monoclinic, <i>C2/c</i>	$Z = 4$
$a = 27.3191$ (12) Å	Mo $K\alpha$ radiation
$b = 18.7841$ (7) Å	$\mu = 1.51$ mm ⁻¹
$c = 12.7375$ (6) Å	$T = 123$ K
	$0.18 \times 0.18 \times 0.04$ mm

Data collection

Oxford Gemini S diffractometer	42490 measured reflections
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)	7387 independent reflections
$T_{\min} = 0.738$, $T_{\max} = 1.000$	5153 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	35 restraints
$wR(F^2) = 0.086$	H-atom parameters constrained
$S = 0.97$	$\Delta\rho_{\max} = 0.85$ e Å ⁻³
7387 reflections	$\Delta\rho_{\min} = -0.25$ e Å ⁻³
313 parameters	

H atoms were positioned geometrically and refined in riding mode, with C–H = 0.98 or 0.99 Å for CH₃ and CH₂ groups, respectively, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups or $1.2U_{\text{eq}}(\text{C})$ for CH₂ groups. The model of the partially occupied hexane solvent molecule

Table 1

Selected geometric parameters (Å, °).

Zn1—O1	1.9829 (14)	Zn2—C14	2.017 (2)
Zn1—N1	1.9866 (18)	Na1—O1	2.3202 (17)
Zn1—C10	2.027 (2)	Na1—N1	2.470 (2)
Zn2—O1	1.9526 (14)	Na1—N2	2.632 (2)
Zn2—O1 ⁱ	1.9706 (14)	Na1—N3	2.562 (2)
O1—Zn1—N1	105.03 (7)	O1—Na1—N2	131.81 (6)
O1—Zn1—C10	115.28 (8)	N1—Na1—N2	123.38 (7)
N1—Zn1—C10	139.69 (8)	N3—Na1—N2	72.21 (6)
O1—Zn2—O1 ⁱ	91.42 (6)	Zn1—O1—Na1	88.36 (6)
O1—Zn2—C14	137.21 (8)	Zn2—O1—Zn1	116.26 (7)
O1 ⁱ —Zn2—C14	131.35 (8)	Zn2 ⁱ —O1—Zn1	117.90 (7)
O1—Na1—N1	82.17 (6)	Zn2—O1—Zn2 ⁱ	88.58 (6)
O1—Na1—N3	127.90 (7)	Zn2—O1—Na1	122.85 (7)
N1—Na1—N3	126.88 (7)	Zn2 ⁱ —O1—Na1	125.94 (7)

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

was restrained with respect to both C—C distances [1.52 (1) Å] and anisotropic displacement parameters. Its occupancy was estimated using the SQUEEZE procedure implemented within PLATON (Spek, 2009). The largest remaining residual electron-density peaks all lie close to the solvent molecule. The largest remaining residual electron-density peaks all lie close to the solvent molecule and thus the occupancy may be slightly underestimated. Four low angle reflections with F_o much greater than F_c were omitted from the final calculations. A small satellite crystal was believed to be present on the sample.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); 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: WQ3004). Services for accessing these data are described at the back of the journal.

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