

**{Bis(3,5-Di-*tert*-butyl-2-oxidobenzyl)-[2-(*N,N*-dimethylamino)ethyl]amine- $\kappa^4 N,N',O,O'$ }zinc(II) and {bis(3-*tert*-butyl-5-methyl-2-oxidobenzyl)-[2-(*N,N*-dimethylamino)ethyl]amine- $\kappa^4 N,N',O,O'$ }(tetrahydrofuran)zinc(II)**

Ruth H. Howard, Manfred Bochmann and Joseph A. Wright\*

School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich NR4 7TJ, England

Correspondence e-mail: joseph.wright@uea.ac.uk

Received 3 May 2006

Accepted 19 May 2006

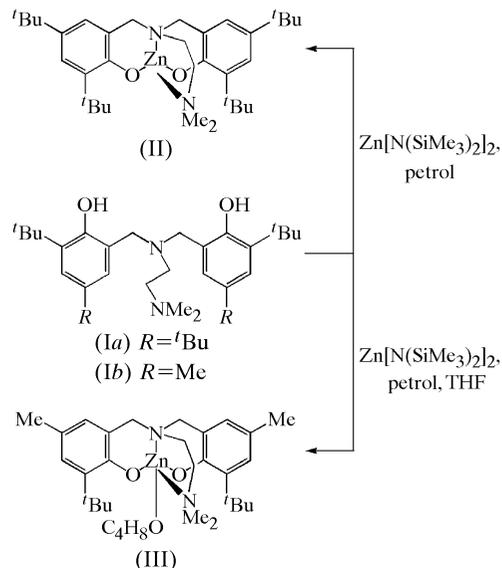
Online 23 June 2006

The title zinc(II) complexes,  $[\text{Zn}(\text{C}_{34}\text{H}_{54}\text{N}_2\text{O}_2)]$ , (II), and  $[\text{Zn}(\text{C}_{28}\text{H}_{42}\text{N}_2\text{O}_2)(\text{C}_4\text{H}_8\text{O})]$ , (III), were obtained as monomeric 1:1 complexes, in contrast with the calcium complexes supported by the same ligand class. Complex (II) crystallizes with two independent molecules in the asymmetric unit, which have similar geometric parameters. The donor atoms in (II) form a distorted trigonal-pyramidal arrangement around the zinc centre. Complex (III) contains a coordinated tetrahydrofuran molecule, resulting in a five-coordinate trigonal-bipyramidal arrangement around the Zn atom. The electron density provided by the coordination of this tetrahydrofuran molecule elongates the Zn–O and Zn–N bonds by approximately 0.07 and 0.10 Å, respectively, in comparison with (II). Neither (II) nor (III) is active as an  $\epsilon$ -caprolactone polymerization catalyst. The data presented here demonstrate that Zn may bind both an ONNO ligand and an additional oxygen-based ligand. The lack of activity is thus not due to steric hindrance at the metal atom.

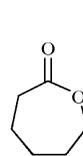
### Comment

The use of biodegradable polymers is of increasing interest, with environmental factors being a key driving force (Drumright *et al.*, 2000). A principle route to these materials is the ring-opening polymerization of  $\epsilon$ -caprolactone (CL) (systematic name: oxepan-2-one) or lactide (LA) (systematic name: 3,6-dimethyl-1,4-dioxane-2,5-dione) to give polyesters. Both of these monomers are readily available from corn, and so are themselves renewable (O'Keefe *et al.*, 2001; Dechy-Cabaret *et al.*, 2004). In order to control the physical properties and tacticity of these polyesters, a variety of main-group and transition metal complexes have attracted attention.

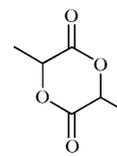
The syntheses of a number of catalysts for CL and LA polymerization based on substituted aminobis(2-hydroxyarylmethyl) (ONNO) ligand systems have recently been



reported (Sarazin *et al.*, 2006). The first complexes of this class of ligands were those of group IV metals; in particular, the titanium, hafnium and zirconium benzyl complexes were structurally characterised and observed to be highly active in the polymerization of  $\alpha$ -olefins (Tshuva *et al.*, 2001*a,b*, 2002; Groyzman *et al.*, 2003). Although Sarazin *et al.* (2006) reported solution data on the magnesium, calcium, titanium and zinc complexes of the ONNO ligand (Ia) ( $R = t\text{Bu}$ ), only the calcium [compound (IV)] and titanium [compound (V)] systems were structurally characterized. The calcium system was found to form a dimeric complex, both in the solid state and in solution. The solid-state structure showed one  $\text{Ca} \cdots \text{H}$  agostic bond at each metal centre ( $\text{Ca} \cdots \text{H}$  distances of 2.31 and 2.41 Å), resulting in distorted octahedral geometry at both Ca atoms. On the other hand, the titanium system was found to be monomeric and six-coordinate, with two coordination sites occupied by  $t\text{PrO}^-$  groups. Equally, solution NMR data for the zinc system, (II), suggested a similar monomeric 1:1 structure. This is in line with the ionic radii of the metal ions, with calcium significantly larger than either titanium or zinc ( $\text{Ca}^{2+} = 1.14$  Å,  $\text{Zn}^{2+} = 0.88$  Å and  $\text{Ti}^{4+} = 0.75$  Å; Atkins *et al.*, 2006). The monomeric nature of the zinc–ONNO complex, (II), has now been established by X-ray analysis. The related complex, (III), bearing a less bulky ONNO ligand, has also been synthesized and characterized for the first time.



$\epsilon$ -caprolactone (CL)

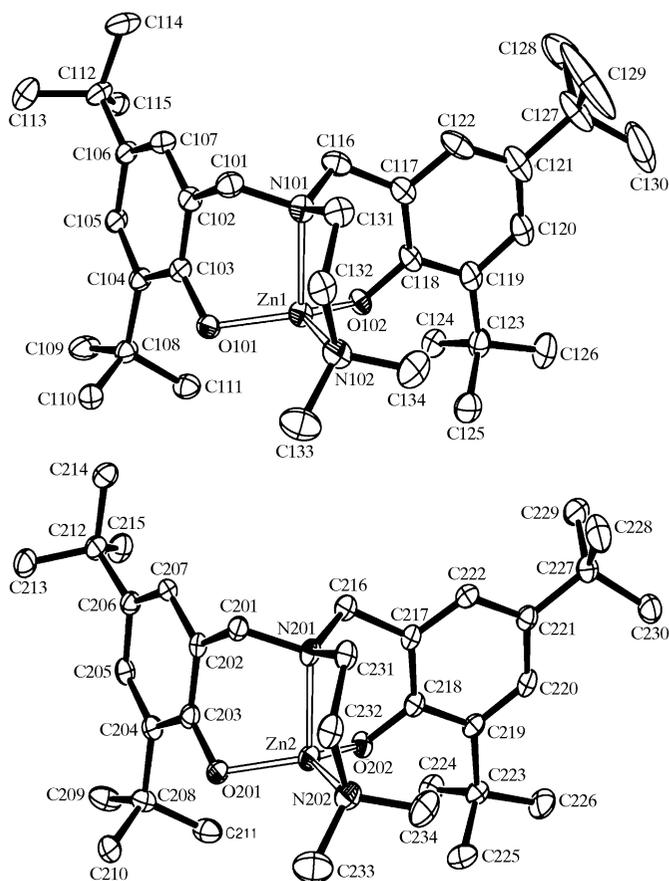


lactide (LA)

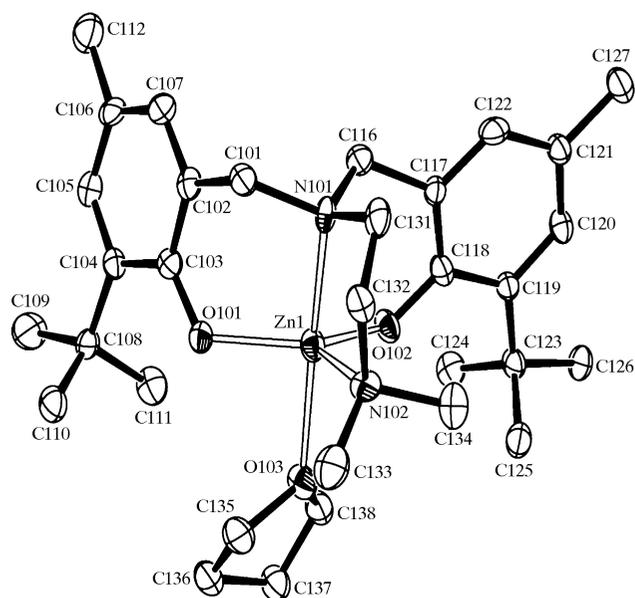
Complex (II) crystallizes in the triclinic space group  $P\bar{1}$ , with two independent molecules in the asymmetric unit

(Fig. 1). Table 1 highlights the bond lengths and angles around the metal centre. It can be seen that the two independent molecules exhibit similar geometric values. The metal–donor distances in (II) (Table 1) are similar to those in the previously reported monomeric titanium complex, (V). The  $M–O$  distances in (II) fall close to those in (V) [1.9034 (15) and 1.9009 (15) Å], consistent with the similar ionic radii of the central atoms. However, the  $M–N$  distances are much longer in the titanium complex [2.400 (2) and 2.335 (2) Å] than in (II). In contrast, the dimeric calcium complex, (IV), exhibits significantly longer (non-bridging)  $M–O$  distances [2.1842 (16) and 2.1817 (16) Å] than (II). The  $M–N$  distances are again significantly shorter in (II) than in (IV) [2.4981 (19)–2.552 (2) Å]. The donor atoms form a distorted trigonal-pyramidal arrangement around the Zn atom, which lies 0.205 (1) Å from mean plane of the O and N atoms which form the base of the pyramid. The  $N_{\text{axial}}–Zn–\text{donor}$  angles demonstrate the distortion of the molecule from ideal geometry, with the two O atoms bent away from the  $Zn–N_{\text{axial}}$  bond.

Complex (III) is trigonal-bipyramidal, with the fifth coordination site occupied by a tetrahydrofuran (THF) molecule



**Figure 1**  
The two independent molecules of (II) in the asymmetric unit, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Both molecules are shown in an arbitrary orientation to allow comparison.



**Figure 2**  
A representation of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

(Fig. 2). The change of  $R$  group from *tert*-butyl to methyl is remote from the metal centre, and so it is reasonable to compare the geometry of (III) with that seen in (II). As expected, the additional electron density donated by the THF molecule results in the elongation of the metal–donor bond lengths in (III) compared with (II) (Tables 1 and 2). The  $Zn–O$  bonds are lengthened by approximately 0.07 Å, whilst the  $Zn–N$  bonds are extended by approximately 0.1 Å. The geometry of the ONNO ligand at the metal centre is similar to that in (II), although the metal atom is displaced by only 0.0185 (16) Å from the mean plane of the equatorial donors.

Neither complex (II) nor (III) is active in the polymerization of LA or CL, in contrast with (IV). The structures presented in this report demonstrate the ability of the metal centre to bind both the ONNO ligand and an additional oxygen-based ligand. The lack of polymerization activity cannot, therefore, be due to steric protection of the Lewis acidic site.

## Experimental

The ligands (Ia) (Tshuva *et al.*, 2001a) and (Ib) (Sarazin *et al.*, 2006) were produced according to literature methods, as was complex (II) (Sarazin *et al.*, 2006). Crystals of (II) suitable for X-ray diffraction were grown from a light petroleum–diethyl ether (1:3 v/v) solution at 268 K. Complex (III) was prepared by a method analogous to that used to produce (II). Reaction of  $Zn[N(\text{SiMe}_3)_2]$  (0.97 g, 2.5 mmol) and (Ib) (1.1 g, 2.5 mmol) in light petroleum (30 ml) gave a white solid.  $^1\text{H NMR}$  (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.31 (*d*, 2H, Ar), 6.60 (*d*, 2H, Ar), 3.76 (*s*, 1H, Ar– $\text{CH}_2$ ), 3.72 (*s*, 1H, Ar– $\text{CH}_2$ ), 3.07 (*d*, 1H, Ar– $\text{CH}_2$ ),

3.03 (*s*, 1H, Ar-CH<sub>2</sub>), 2.34 (*s*, 6H, 2 × MeAr), 2.04 (*t*, 1H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 1.76 (*s*, 18H, <sup>t</sup>Bu), 1.59 (*t*, 1H, N-CH<sub>2</sub>-CH<sub>2</sub>-N), 1.49 (*s*, 6H, NMe<sub>2</sub>); <sup>13</sup>C NMR (75MHz, C<sub>6</sub>D<sub>6</sub>): δ 164.9 (C-O), 138.7 (C<sub>Ar</sub>), 130.5 (C<sub>Ar</sub>), 128.9(C<sub>Ar</sub>), 123.0 (C<sub>Ar</sub>), 122.9 (C<sub>Ar</sub>), 60.1 (Ar-CH<sub>2</sub>), 59.4 (N-CH<sub>2</sub>), 46.5 (N-CH<sub>2</sub>), 41.8 [N(CH<sub>3</sub>)<sub>2</sub>], 35.8 [C(CH<sub>3</sub>)<sub>3</sub>], 30.2 [C(CH<sub>3</sub>)<sub>3</sub>], 22.9 (Ar-CH<sub>3</sub>). Crystals of (III) suitable for X-ray diffraction were grown from a tetrahydrofuran–light petroleum–diethyl ether solution (1:1:3 *v/v/v*) at 268 K.

### Compound (II)

#### Crystal data

[Zn(C<sub>34</sub>H<sub>54</sub>N<sub>2</sub>O<sub>2</sub>)]  
*M<sub>r</sub>* = 588.16  
 Triclinic, *P1*  
*a* = 12.9275 (12) Å  
*b* = 14.0002 (13) Å  
*c* = 19.6729 (14) Å  
 α = 100.747 (7)°  
 β = 102.467 (7)°  
 γ = 96.879 (8)°  
*V* = 3367.8 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.160 Mg m<sup>-3</sup>  
 Mo *Kα* radiation  
 μ = 0.76 mm<sup>-1</sup>  
*T* = 140 (1) K  
 Plate, colourless  
 0.20 × 0.08 × 0.02 mm

#### Data collection

Oxford Xcalibur-3 CCD area-detector diffractometer  
 Thin-slice φ and ω scans  
 Absorption correction: multi-scan (ABSPACK; Oxford Diffraction, 2003)  
*T<sub>min</sub>* = 0.925, *T<sub>max</sub>* = 0.983  
 42426 measured reflections  
 15272 independent reflections  
 8001 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.076  
*θ<sub>max</sub>* = 27.6°

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.042  
*wR* (*F*<sup>2</sup>) = 0.071  
*S* = 0.79  
 15272 reflections  
 744 parameters  
 H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0243*P*)<sup>2</sup>]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.45 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.43 e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °) for (II).

Zn1—O101	1.8918 (15)	Zn2—O201	1.8821 (16)
Zn1—O102	1.8960 (17)	Zn2—O202	1.8899 (17)
Zn1—N101	2.065 (2)	Zn2—N201	2.0643 (18)
Zn1—N102	2.0864 (19)	Zn2—N202	2.0727 (19)
O101—Zn1—O102	125.35 (7)	O201—Zn2—O202	121.39 (7)
O101—Zn1—N101	99.58 (7)	O201—Zn2—N201	99.95 (7)
O102—Zn1—N101	99.77 (7)	O202—Zn2—N201	99.80 (7)
O101—Zn1—N102	112.76 (7)	O201—Zn2—N202	113.08 (8)
O102—Zn1—N102	118.59 (8)	O202—Zn2—N202	122.20 (8)
N101—Zn1—N102	87.81 (8)	N201—Zn2—N202	88.07 (7)

### Compound (III)

#### Crystal data

[Zn(C<sub>28</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub>)(C<sub>4</sub>H<sub>8</sub>O)]  
*M<sub>r</sub>* = 576.11  
 Monoclinic, *P2<sub>1</sub>/c*  
*a* = 13.669 (3) Å  
*b* = 17.476 (4) Å  
*c* = 12.989 (4) Å  
 β = 93.14 (2)°  
*V* = 3098.1 (14) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.235 Mg m<sup>-3</sup>  
 Mo *Kα* radiation  
 μ = 0.83 mm<sup>-1</sup>  
*T* = 140 (1) K  
 Block, light yellow  
 0.06 × 0.06 × 0.02 mm

#### Data collection

Oxford X-calibur-3 CCD area-detector diffractometer  
 Thin-slice φ and ω scans  
 Absorption correction: multi-scan (ABSPACK; Oxford Diffraction, 2003)  
*T<sub>min</sub>* = 0.801, *T<sub>max</sub>* = 0.984  
 33137 measured reflections  
 7121 independent reflections  
 2308 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.195  
*θ<sub>max</sub>* = 27.8°

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.049  
*wR* (*F*<sup>2</sup>) = 0.073  
*S* = 0.68  
 7121 reflections  
 353 parameters  
 H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0123*P*)<sup>2</sup>]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.37 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.49 e Å<sup>-3</sup>

**Table 2**

Selected geometric parameters (Å, °) for (III).

Zn1—O102	1.958 (2)	Zn1—N102	2.166 (3)
Zn1—O101	1.961 (2)	Zn1—O103	2.246 (3)
Zn1—N101	2.163 (3)		
O102—Zn1—O101	127.59 (10)	N101—Zn1—N102	82.88 (12)
O102—Zn1—N101	93.35 (11)	O102—Zn1—O103	91.02 (10)
O101—Zn1—N101	94.41 (10)	O101—Zn1—O103	87.46 (9)
O102—Zn1—N102	112.67 (11)	N101—Zn1—O103	172.77 (11)
O101—Zn1—N102	119.71 (11)	N102—Zn1—O103	90.13 (11)

All H atoms were refined using a riding model, with C—H = 0.98–0.99 Å and *U<sub>iso</sub>*(H) = 1.5 or 1.2 times *U<sub>eq</sub>*(C). Methyl H atoms were positioned using residual electron density (HFIX 137). One *tert*-butyl group of (II) (central atom C112, and methyl atoms C113, C114 and C115) was found to be disordered and was freely refined over two positions. This gave a final occupancy of 0.853 (3) for the major position (shown in Fig. 2). The central atom-to-methyl bonds were restrained to a distance of 1.55 Å for all of the disordered C atoms (DFIX 1.55 0.02). A second *tert*-butyl group (central atom C127, and methyl atoms C128, C129 and C130) showed evidence of disorder, particularly in the displacement parameters for atom C129. However, this could not be successfully modelled.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED*; data reduction: *CrysAlis RED*; 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); software used to prepare material for publication: *SHELXL97*, *PLATON* (Spek, 2003), *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

RHH and JAW thank the EPSRC for funding.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3023). Services for accessing these data are described at the back of the journal.

### References

- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.  
 Altomare, A., Casciarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

- Atkins, P. W., Overton, T., Rourke, J., Weller, M. & Armstrong, F. (2006). *Shriver & Atkins Inorganic Chemistry*, 4th ed. Oxford University Press.
- Dechy-Cabaret, O., Martin-Vaca, B. & Bourissou, D. (2004). *Chem. Rev.* **104**, 6147–6176.
- Drumright, R. E., Gruber, P. R. & Henton, D. E. (2000). *Adv. Mater.* **12**, 1841–1846.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Groysman, S., Goldberg, I., Kol, M., Genizi, E. & Goldschmidt, Z. (2003). *Inorg. Chim. Acta*, **345**, 137–144.
- O'Keefe, B. J., Hillmyer, M. A. & Tolman, W. B. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2215–2224.
- Oxford Diffraction (2003). *ABSPACK*, *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Sarazin, Y., Howard, R. H., Hughes, D. L., Humphrey, S. M. & Bochmann, M. (2006). *Dalton Trans.* pp. 340–350.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Tshuva, E. Y., Goldberg, I., Kol, M. & Goldschmidt, Z. (2001a). *Inorg. Chem.* **40**, 4263–4270.
- Tshuva, E. Y., Goldberg, I., Kol, M. & Goldschmidt, Z. (2001b). *Chem. Commun.* pp. 2120–2121.
- Tshuva, E. Y., Groysman, S., Goldberg, I., Kol, M. & Goldschmidt, Z. (2002). *Organometallics*, **21**, 662–670.