Bis[4-(1-ethylpropylimino)pentan-2-onato]-zinc(II)

J.S. Matthews,* T. S. Ouattara and R. J. Butcher

Howard University, Department of Chemistry, 525 College Street, N.W., Washington DC 20059, USA

Correspondence e-mail:
jsmatthews@howard.edu

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.023
wR factor = 0.061
Data-to-parameter ratio = 25.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Zn(C_{10}H_{18}NO)_2]$, is a monomeric homoleptic zinc complex. The Zn atom occupies the center of a distorted tetrahedral environment and is coordinated by two O atoms [Zn—O = 1.9468 (9) and 1.9484 (10) Å] and two N atoms [Zn—N = 2.0142 (12) and 2.0149 (11) Å].

Comment

Zinc oxide is a versatile material that finds applications in the fabrication of sensors, varistors, surface acoustic wave devices and photo- and electroluminescent devices (Polarz *et al.*, 2005). Significant effort has been directed toward the exploitation of the properties of the wide band gap (3.37 eV) and large exciton binding energy (60 meV) of this unique semiconducting metal oxide. The growth of high quality ZnO has been achieved *via* several different methods, including metal-organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE) and pulsed-laser deposition (PLD) (Yak *et al.*, 2005). MOCVD is the most attractive method for the growth of ZnO due to the capability for large area growth, precise control of film thickness, and good conformal coverage. MOCVD requires the use of a suitable precursor for efficient growth of the desired material. The precursor chemistry of ZnO has included many ligand platforms ranging from alkoxides (Boyle *et al.*, 2004) and amides (Gaul *et al.*, 2000) to β-diketonates (Babcock *et al.*, 2000). We have recently investigated the utility of the β-ketoiminate ligand platform for use as a source material in the growth of high quality ZnO. Toward this end, we have successfully synthesized the title compound, (I).

(I)
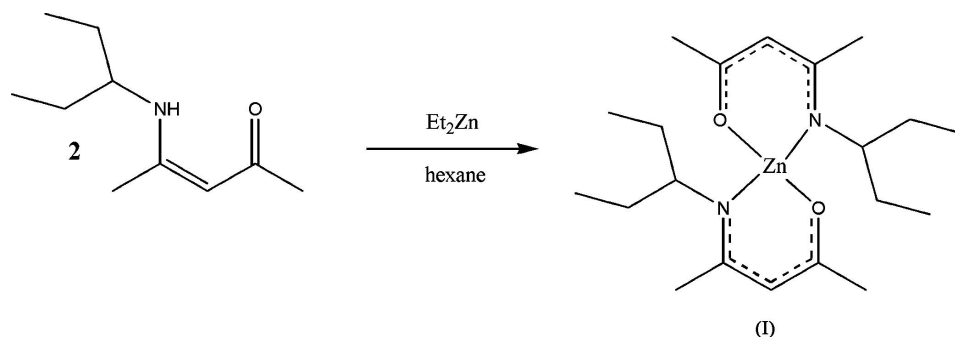
The present single-crystal *X*-ray diffraction study shows the title compound to be monomeric in the solid state (Fig. 1), crystallizing in space group $P2_1/c$. The Zn atom occupies the center of a slightly distorted tetrahedral environment and is coordinated by two O atoms and two N atoms (Table 1). Due to the paucity of structural data for zinc β-ketoiminates, the
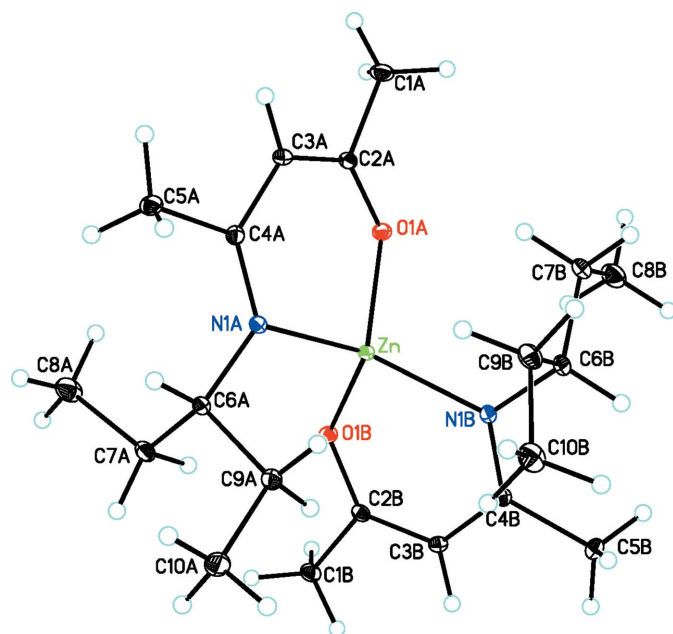
Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as spheres of arbitrary radius.

Zn—O and Zn—N bonds were compared to analogous bonds encountered in zinc bis-salicylaldiminato (Darensbourg *et al.* 2001), diiminate (Cheng *et al.*, 2001) and diketonate complexes (Harbach *et al.*, 2003, Bridson *et al.*, 2006). The Zn—O bond lengths for the present study are shorter than those observed for the analogous monomeric zinc β-diketo-nates, Zn(acac)$_2$·H$_2$O and [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Zn(acac)], which exhibit bond lengths of 2.035 and 1.961 Å, respectively. The Zn—O bonds are, however, longer than those reported for the non-halogenated monomeric bis(salicylaldiminato)zinc complexes. The Zn—N bond distances are intermediate between the Zn—N values reported for zinc diiminate complexes. The N—Zn—O bite angles are larger than the 92.6 and 92.9° observed for the β-diiminate.

Experimental

Under an inert atmosphere of nitrogen, 4-(*N*-1-ethylpropyl-amino)pent-3-en-2-one (0.92 g, 5.44 mmol) was added to a Schlenk flask containing 50 ml of dry hexane and a magnetic stir bar. The mixture was stirred and cooled to 273 K. A solution of 1*M* diethylzinc in hexane (3.00 ml, 3.00 mmol) was added *via* a syringe. The mixture was allowed to warm to room temperature with stirring for 1 h. The solvent was removed under reduced pressure to afford a white solid. The isolated solid was dissolved in dry pentane and held at 268 K for two days, at which time the formation of colorless crystals was observed. Spectroscopic analysis: ^{1}H NMR (CDCl$_3$, δ, p.p.m.): 1.25, 1.33 [*t*, 6H, 6H, (C**H**$_3$CH$_2$)], 1.74, 1.83 (*m*, 4H, 4H, CH$_3$C**H**$_2$), 1.92 (*s*, 6H, CH$_3$CN), 1.97 (*s*, 6H, CH$_3$CO), 3.35 (*m*, 2H, C**H**N), 4.89 (*s*, 2H, COC**H**CN); ^{13}C NMR (CDCl$_3$, δ, p.p.m.): 19.15 ([CH$_3$CN], 10.26 (CH$_3$CH$_2$), 28.50 (CH$_3$CH$_2$), 28.67 (CH$_3$CO), 63.42 (CHNH), 96.66 (COCHCN), 170.83 (CH$_3$CN), 181.98 (CH$_3$CO).

Crystal data

[Zn(C$_{10}$H$_{18}$NO)$_2$]
$M_r = 401.88$
Monoclinic, $P2_1/c$
$a = 8.355$ (4) Å
$b = 12.638$ (6) Å
$c = 20.402$ (10) Å
$\beta = 98.544$ (7)°
$V = 2130.4$ (18) Å^3
$Z = 4$

$D_x = 1.253$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9082 reflections
$\theta = 2.6$–30.3°
$\mu = 1.17$ mm^{-1}
$T = 293$ (2) K
Chunk, colorless
$0.50 \times 0.50 \times 0.35$ mm

Data collection

Bruker SMART 1K CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{min} = 0.554$, $T_{max} = 0.665$
30574 measured reflections

5972 independent reflections
5454 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 30.2°$
$h = -11 \rightarrow 10$
$k = -16 \rightarrow 17$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.061$
$S = 1.03$
5972 reflections
234 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 0.723P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—O1B	1.9468 (9)	O1B—C2B	1.2915 (13)
Zn—O1A	1.9484 (10)	N1A—C4A	1.3166 (14)
Zn—N1A	2.0142 (12)	N1A—C6A	1.4815 (14)
Zn—N1B	2.0149 (11)	N1B—C4B	1.3157 (14)
O1A—C2A	1.2930 (14)	N1B—C6B	1.4825 (14)
O1B—Zn—O1A	112.45 (4)	C2B—O1B—Zn	119.77 (7)
O1B—Zn—N1A	110.01 (4)	C4A—N1A—C6A	120.71 (9)
O1A—Zn—N1A	97.56 (4)	C4A—N1A—Zn	120.17 (7)
O1B—Zn—N1B	97.83 (4)	C6A—N1A—Zn	119.12 (6)
O1A—Zn—N1B	112.89 (4)	C4B—N1B—Zn	119.48 (7)
N1A—Zn—N1B	126.57 (4)	C6B—N1B—Zn	119.76 (7)
C2A—O1A—Zn	120.39 (7)		

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry with C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C), but each group was allowed to rotate freely about its C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.95–1.00 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

References

Babcock, J. R., Wang, A., Edleman, N. L., Benson, D. D., Metz, A. W., Metz, M. V. & Marks, T. J. (2000). *MRS Proceedings*, **623**, 317–328.

Boyle, T. J., Bunge, S. D., Andrews, N. L., Matzen, L. E., Sieg, K., Rodriguez, M. A. & Headley, T. J. (2004). *Chem. Mater.* **16**, 3279–3288.

Bridson, J. H., Henderson, W., Nicholson, B. K. & Andy Hor, T. S. (2006). *Inorg. Chim. Acta*, **359**, 680–684.

Bruker (2001). *SMART* (Version 5.624) and *SAINT* (Version 6.04). Bruker AXS Inc., Madison, Wisconsin, USA.

Cheng, M., Moore, D. R., Reczek, J. J., Chamberlain, B. M., Lobkovsky, E. B. & Coates, G. W. (2001). *J. Am. Chem. Soc.* **123**, 8738–8749.

Darensbourg, D. J., Rainey, P. & Yarbrough, J. (2001). *Inorg. Chem.* **40**, 986–993.

Gaul, D. A., Just, O. & Rees, W. S. Jr (2000). *Inorg. Chem.* **39**, 5648–5654.

Harbach, P., Lerner, H. W. & Bolte, M. (2003). *Acta Cryst.* E**59**, m724–m725.

Polarz, S., Roy, A., Merz, M., Halm, S., Schroder, D., Schneider, L., Bacher, G., Kruis, F. E. & Dreiss, M. (2005). *Small*, **1**, 540–552.

Sheldrick, G. M. (1997a). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1997b). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2002). *SADABS*. University of Göttingen, Germany.

Yak, Y., Yong, K. & Park, C. (2005). *J. Cryst. Growth*, **285**, 549–554.