

Diisopropyl(*N,N,N',N'*-tetramethylethylenediamine)zinc(II), the first crystal structure of a diisopropylzinc complex

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Key indicators

Single-crystal X-ray study

T = 100 K

Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$

R factor = 0.024

wR factor = 0.065

Data-to-parameter ratio = 20.2

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

Although diisopropylzinc has attracted considerable interest as a useful organometallic reagent over the past ten years, diisopropylzinc complexes are still absent in the present version of the Cambridge Structural Database. In the title compound, a tmeda (tmeda is *N,N,N',N'*-tetramethylethylenediamine) adduct, $[\text{Zn}(\text{C}_3\text{H}_7)_2(\text{C}_6\text{H}_{16}\text{N}_2)]$, the Zn^{II} atom, which lies on a crystallographic twofold rotation axis, is in a distorted tetrahedral geometry. The molecules are held together by dispersion forces, without any contacts within the sum of the van der Waals radii.

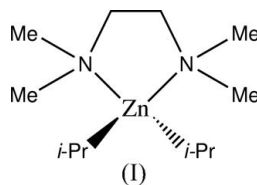
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Comment

The first report on the preparation of diisopropylzinc was published by Gladstone & Tribe (1873), but yields were low until a modified synthetic method was published by Sooros & Morgana (1944). Today, diisopropylzinc is commercially available as a 1.0 M solution in toluene, and diisopropylzinc has become an important reagent in modern synthetic organic chemistry. Two recent examples of the use of diisopropylzinc are the preparation of organozinc reagents containing carbonyl functions by lithium acetylacetonate-catalysed zinc-iodine exchange of functionalized aryl iodides with diisopropylzinc (Kneisel, *et al.*, 2004), and the boron-zinc exchange, which enables hydroboration followed by conversion into the corresponding zinc derivative with retention of stereochemistry (Hupe *et al.*, 2003). The most remarkable use of diisopropylzinc is in the Soai asymmetric autocatalytic reaction (Soai *et al.*, 1995), in which diisopropylzinc reacts with prochiral pyrimidyl-5-carbaldehydes, a reaction that is catalysed by the chiral zinc alkoxide formed.

The most recent contribution to the subject is the autocatalytic addition of diisopropylzinc to 2-ferrocenylethynylpyrimidine-5-carbaldehyde, a reaction with a positive non-linear effect (Lutz *et al.*, 2006). From this point of view, it is



noteworthy that no crystal structures of diisopropylzinc complexes are to be found in the Cambridge Structural Database (CSD; Version 5.27, November 2005; Allen 2002); the only structure in the CSD of an *i*-Pr-Zn compound is an isopropylzinc bis(trimethylsilyl)phosphide complex (Rademacher, *et al.*, 1995). The structure of an *N,N,N',N'*-tetra-

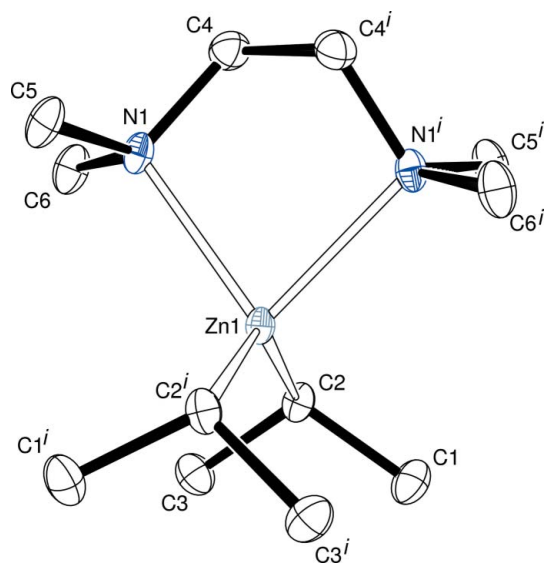


Figure 1
The molecular structure of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted. [Symmetry code (i): $-x, y, \frac{1}{2} - z$.]

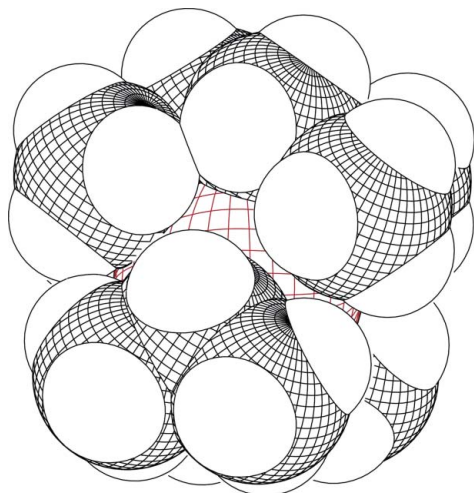


Figure 2
A space-filling plot, showing the non-polar nature of (I). The orientation of the molecule is about the same as in Fig. 1. All polar structural motifs are shielded inside the molecule, and the molecular surface consists of alkyl groups. Therefore, (I) is soluble in hydrocarbon solvents and does not display any short contacts in the crystalline state.

methylethylenediamine (tmeda) adduct of diisopropylzinc, (I) (Fig. 1), is presented here.

The coordination geometry around the central Zn atom in (I) (Fig. 1), which lies on a crystallographic twofold axis, is distorted tetrahedral, where the diisopropylzinc unit is distorted towards a linear arrangement (Boersma, 1982). The C—Zn—C angle in (I) is $130.46(8)^\circ$, which is similar to the corresponding value of $135.8(3)^\circ$ in $[\text{Zn}(\text{CH}_3)_2(\text{tmeda})]$ (O'Brian *et al.*, 1993). There are two more $[\text{ZnR}_2(\text{tmeda})]$ complexes in the CSD, where R is a purely aliphatic alkyl group. The C—Zn—C angles in $[\text{Zn}(\text{CH}_2\text{CH}_3)_2(\text{tmeda})]$ (Andrews *et al.*, 1998), and $[\text{Zn}\{\text{CH}_2\text{C}(\text{CH}_3)_3\}_2(\text{tmeda})]$ (O'Brian *et al.*, 1993), are $118(1)$ and $148(5)^\circ$, respectively.

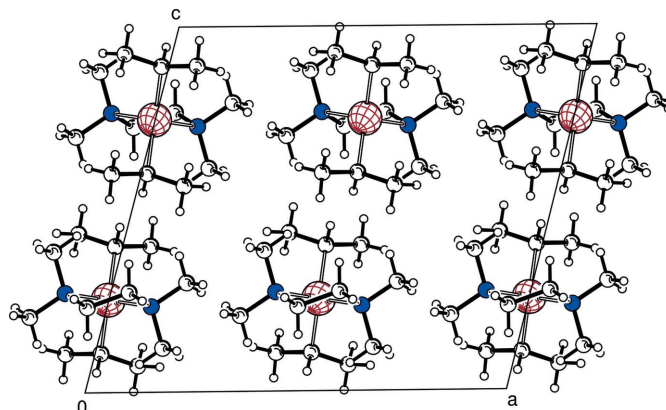


Figure 3
The crystal packing in (I).

The crystal structure of (I) does not display any intermolecular interactions that are within the sum of the van der Waals radii. As can be seen from Fig. 2, the molecules display a 'hydrophobic' surface with all polar Zn—C and Zn—N bonds effectively shielded inside the molecule. The crystal packing of (I) is visualized in Fig. 3.

Experimental

All operations, except the preparation of the zinc–copper couple, were carried out under a nitrogen atmosphere using Schlenk glassware, dried at 403 K for 12 h. Commercial isopropyl bromide (E. Merck) and isopropyl iodide (Aldrich) were used without further purification. A zinc–copper couple was prepared according to Fieser & Fieser (1967) from zinc powder (Riedel-deHaën) and copper sulfate pentahydrate (Kebo). Hexane was distilled from sodium/benzophenone/tetraglyme shortly prior to use.

Diisopropylzinc was prepared according to previously published procedures (Sooros & Morgana, 1944). A mixture of isopropyl iodide (20.0 ml, 0.20 mol) and isopropyl bromide (18.8 ml, 0.20 mol) was prepared and 2 ml was added to the zinc–copper couple (42.3 g, 0.63 mol zinc) at 333 K. The temperature was raised to 368 K and within 5 min white fumes appeared. The rest of the halide mixture was added dropwise at ambient temperature over a period of 3 h, and the reaction mixture was stirred overnight. The reaction mixture was evaporated at ambient temperature and 10^{-2} mbar to remove excess alkyl halides. As the temperature was raised to 373 K, the product distilled over as a clear colourless liquid. The distillation was completed at 413 K (yield 25.2 g, 83%).

N,N,N',N' -Tetramethylethylenediamine (0.36 ml, 2.4 mmol) was added to diisopropylzinc (0.3 ml, 2.4 mmol), resulting in a white precipitate. The precipitate was dissolved in hexane (3 ml) with gentle heating. After a few hours at ambient temperature, colourless needle-shaped crystals of diisopropyl- $(N,N,N',N'$ -tetramethylethylenediamine)zinc(I) appeared (yield 0.42 g, 67%).

Crystal data

$[\text{Zn}(\text{C}_3\text{H}_7)_2(\text{C}_6\text{H}_{16}\text{N}_2)]$
 $M_r = 267.75$
 Monoclinic, $C2/c$
 $a = 14.370(4) \text{ \AA}$
 $b = 8.5935(16) \text{ \AA}$
 $c = 12.684(3) \text{ \AA}$
 $\beta = 104.928(8)^\circ$
 $V = 1513.4(6) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.175 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 1.60 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Needle, colourless
 $0.2 \times 0.08 \times 0.08 \text{ mm}$

Data collection

Rigaku R-AXIS IIC image-plate system diffractometer
 φ scans
 Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
 $T_{\min} = 0.724$, $T_{\max} = 0.883$

5464 measured reflections
 1477 independent reflections
 1407 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 27.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.065$
 $S = 1.09$
 1477 reflections
 73 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.2577P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.71 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.52 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C2–Zn1	2.0318 (14)	N1–Zn1	2.2804 (13)
C2–Zn1–C2 ⁱ	130.46 (8)	C2–Zn1–N1 ⁱ	107.88 (5)
C2–Zn1–N1	109.19 (5)	N1–Zn1–N1 ⁱ	81.31 (7)

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

All H atoms were placed in calculated positions, with C–H = 0.96–0.98 Å, and included in the final cycles of refinement using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

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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References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
 Andrews, P. C., Raston, C. L., Skelton, B. W. & White, A. H. (1998). *Organometallics*, **17**, 779–782.
 Boersma, J. (1982). *Comprehensive Organometallic Chemistry 2*, p. 825. Oxford: Pergamon Press Ltd.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Fieser, L. F. & Fieser, M. (1967). *Reagents for Organic Synthesis*, p. 1292. New York: John Wiley and Sons Inc.
 Gladstone, J. H. & Tribe, A. (1873). *J. Chem. Soc.* **26**, 961–970.
 Hupe, E., Calaza, M. I. & Knochel, P. (2003). *Chem. Eur. J.* **9**, 2789–2796.
 Kneisel, F. F., Dochnahl, M. & Knochel, P. (2004). *Angew. Chem. Int. Ed.* **43**, 1017–1021.
 Lutz, F., Kawasaki, T. & Soai, K. (2006). *Tetrahedron Asymmetry*, **17**, 486–490.
 O'Brian, P., Hursthouse, M. B., Motevalli, M., Walsh, J. R. & Jones, A. C. (1993). *J. Organomet. Chem.* **449**, 1–8.
 Rademacher, B., Schwarz, W. & Westerhausen, M. (1995). *Z. Anorg. Allg. Chem.* **621**, 287–300.
 Rigaku (2000). *CrystalClear*. Version 1.3. Rigaku Corporation, Tokyo, Japan.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Soai, K., Shibata, T., Morioka, H. & Choji, K. (1995). *Nature (London)*, **378**, 767–???.
 Sooros, H. & Morgana, M. (1944). *J. Am. Chem. Soc.* **66**, 893–894.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.