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Dichloro(2,3,6,8,11,12,15,17-octamethyl-5,9,14,18-tetraazadibenzo[*a*,*h*]cyclotetradecene-κ^4N)zirconium(IV) tetrahydrofuran hemisolvate

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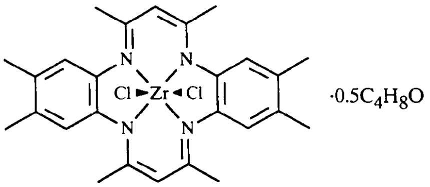
Abstract

The coordination geometry of the title compound, $[ZrCl_2(C_{26}H_{30}N_4)]\cdot0.5C_4H_8O$, approximates to trigonal prismatic. The Cl atoms are coordinated to the zirconium in a *cis* configuration. Disordered tetrahydrofuran (THF) solvent molecules are present in the crystal structure.

Comment

New ligand systems for olefin polymerization are currently of great interest (Bochmann, 1996) and the title complex, (I), was synthesized in the course of our research into improved Ziegler–Natta polymerization catalysts. The structure was determined as part of a general study to test the thesis that *cis*-dihalides are better catalysts than the corresponding *trans* isomers.



(I)

The structure of (I) is illustrated in Fig. 1. The Cl atoms are in a *cis* configuration, with an inter-bond angle of 84.79 (8)°, and have Zr—Cl bond lengths of 2.495 (2) and 2.508 (3) Å. The coordination geometry is approximately trigonal prismatic, with the pseudo-threefold axis passing through the centre of the N1/N2/Cl1 triangle and the Zr atom. The coordinated N-macrocycle retains its 'free' saddle shape (Alcock *et al.*, 1994) and the four N-donor atoms are almost coplanar (r.m.s. deviation 0.02 Å). The plane formed by the Zr1, Cl1 and Cl2 atoms is inclined at 83.1 (1)° to the N_4 plane; an angle of 90° would be required for a regular trigonal prismatic structure. The Zr atom is displaced from the N_4 plane by 1.061 (3) Å, a distance comparable with that of 1.070 (2) Å in $[Ti(C_{22}H_{22}N_4)Cl_2]$ (De Angelis *et al.*, 1992).

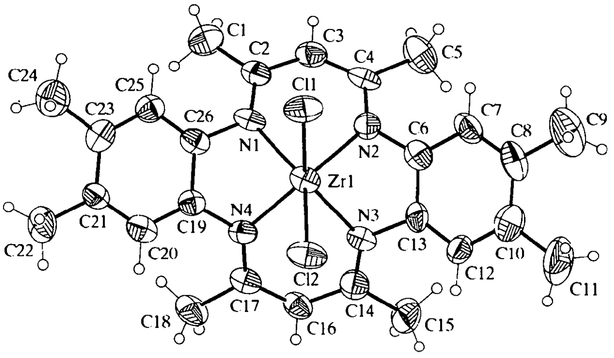


Fig. 1. View of the title molecule showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

LiMe (1.2 mol dm^{-3} solution in Et_2O, 2.2 mmol) was added dropwise to a solution of the protonated ligand H_2omtaa ($C_{26}H_{32}N_4$; 0.5 g, 1.1 mmol) at 195 K. The resultant red solution was stirred at 313–323 K for 3.5 h. The Li_2[omtaa] solution was transferred to a solution of $[ZrCl_4(thf)_2]$ (1.1 mmol) in Et_2O (30 ml). The suspension was heated gently at 308 K for 5 h and the resultant solid which formed was collected, washed with hexane and dried *in vacuo* (yield 50%). Analysis calculated for $C_{26}H_{30}Cl_2N_4Zr$: C 55.70, H 5.39, N 9.99%; found: C 55.91, H 5.43, N 10.24%; ^1H NMR ($CDCl_3$, 250 MHz): 7.38 (*s*, 4H), 5.59 (*s*, 2H), 2.36 (*s*, 12H), 2.47 (*s*, 12H); ^{13}C NMR ($CDCl_3$, 250 MHz): 158.22, 139.02, 126.73, 125.89, 105.08, 22.77, 20.25. The compound was recrystallized from THF.

Crystal data

$[ZrCl_2(C_{26}H_{30}N_4)]\cdot0.5C_4H_8O$
$M_r = 596.71$
Triclinic
$P\bar{1}$
$a = 8.958\ (5)$ Å
$b = 13.258\ (7)$ Å
$c = 14.769\ (8)$ Å
$\alpha = 71.61\ (5)°$
$\beta = 88.37\ (4)°$
$\gamma = 70.53\ (4)°$
$V = 1563.5\ (15)$ Å^3
$Z = 2$
$D_x = 1.267$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 250 reflections
$\theta = 1.86$–$24.88°$
$\mu = 0.545$ mm^{-1}
$T = 150\ (2)$ K
Block
$0.18 \times 0.14 \times 0.07$ mm
Colourless

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Data collection

Delft Instruments FAST TV area-detector diffractometer
ω scans
Absorption correction: none
6191 measured reflections
4062 independent reflections
1723 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.070$
$\theta_{\rm max} = 24.88°$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 9$
$l = -17 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.117$
$S = 0.709$
4062 reflections
346 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.421$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.289$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zr1—N4	2.154 (5)	Zr1—N3	2.168 (6)
Zr1—N1	2.163 (6)	Zr1—Cl1	2.495 (2)
Zr1—N2	2.164 (6)	Zr1—Cl2	2.508 (3)
N4—Zr1—N1	74.2 (2)	N2—Zr1—Cl1	89.68 (17)
N4—Zr1—N2	122.3 (2)	N3—Zr1—Cl1	142.76 (16)
N1—Zr1—N2	77.6 (3)	N4—Zr1—Cl2	88.29 (17)
N4—Zr1—N3	78.5 (2)	N1—Zr1—Cl2	144.20 (19)
N1—Zr1—N3	120.1 (2)	N2—Zr1—Cl2	137.06 (19)
N2—Zr1—N3	74.0 (2)	N3—Zr1—Cl2	85.19 (16)
N4—Zr1—Cl1	136.78 (19)	Cl1—Zr1—Cl2	84.79 (8)
N1—Zr1—Cl1	87.18 (16)		

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). Data were collected from 0.2° ω-rotation exposures of 10 s each, with a crystal-to-detector distance of 49.37 (8) mm. Coverage of the unique set was over 74% complete to at least 25° in θ. Crystal decay was found to be negligible by comparison of intensities of repeated reflections. H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached. The disordered THF solvent was modelled as two partially occupied positions with occupancies of 0.25 and with some distance restraints.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1992). Cell refinement: *MADNES*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1287). Services for accessing these data are described at the back of the journal.

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Bis[*N*-benzoyl-*N*′-(2-pyridylmethylene)hydrazine]trinitratocerium(III) acetone dihydrate†

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Abstract

The crystal structure of the title compound, $[Ce(NO_3)_3(C_{13}H_{11}N_3O)_2]\cdot C_3H_6O\cdot 2H_2O$, has been determined. The Ce^{III} atom is 12-coordinate by linking to two tridentate 2-pyridinecarboxaldehyde benzoylhydrazone ligands and three bidentate nitrate ligands. The Ce—O distances range between 2.528 (3) and 2.759 (4) Å, and the Ce—N distances range between 2.725 (4) and 2.848 (4) Å. All the water molecules are involved in hydrogen-bond formation with the Ce-containing molecules.

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† Alternative name: tris(nitrato-*O*,*O*′)bis{*N*-[(2-pyridyl-*N*)methyleneamino-*N*]benzamide-*O*}cerium(III) acetone dihydrate.

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