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[1,2-Bis(2-methoxyethyl-*O*)-η^5-cyclopentadienyl]trichlorozirconium(IV)

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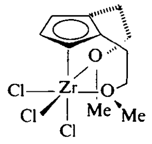
Abstract

The monomeric title compound, [$ZrCl_3(C_{11}H_{17}O_2)$], has a pseudo-octahedral structure. The tridentate ligand contains a cyclopentadienyl ring bearing two 1,2-substituted ether side chains that are forced into a unique facial η^5:η^1:η^1 arrangement. The three Cl atoms occupy the other facial positions. The asymmetric unit contains two independent but almost identical molecules.

Comment

In the last decade, interest in cyclopentadienyl (Cp) ligands bearing functional groups capable of intramolecular coordination has increased enormously (Jutzi *et al.*, 1996). However, only a few examples exist in which two such substituents are attached to the Cp ring (Fryzuk *et al.*, 1993, 1995; Atherton *et al.*, 1995; Mu *et al.*, 1996) and, to the best of our knowledge, only one structure is known in which these substituents are adjacent (1,2) to one another (Barthel-Rosa *et al.*, 1995, 1996). We report here the first structure of a zirconium compound complexed to a 1,2-disubstituted cyclopentadienyl ligand bearing two intramolecular coordinating ether groups, (I).



(I)

The unit cell contains two independent molecules which are identical within error limits and so only one of them will be discussed (Fig. 1).

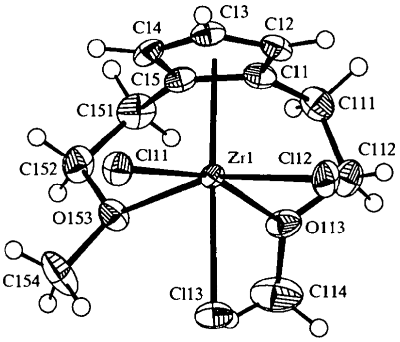


Fig. 1. *DIAMOND* plot (Brandenburg, 1996) (50% probability) of the title compound with the atomic numbering scheme. Only one of the two independent molecules is shown.

The molecule adopts a monomeric pseudo-octahedral structure. The title complex, (I), contains a Cp ring which has two ether side chains substituted in a 1,2-fashion. The tridentate ligand is bonded in a facial η^5:η^1:η^1 arrangement as a result of geometrical constraints. The three Cl atoms occupy the other facial positions. Normally, complexes of type $CpZrCl_3(L)_2$ exhibit a *cis,mer* arrangement of ligands (Erker *et al.*, 1990; Erker, 1990; Wells *et al.*, 1981). Mu and co-workers (Mu *et al.*, 1995) prepared a zirconium trichloride compound bearing a Cp ligand containing one substituent with two donor atoms that is coordinated in a meridional η^5:η^1:η^1-fashion.

There is a slight asymmetry in the η^5-bonding of the Cp unit. The Zr—C bond length progressively increases from C14 and C15 [2.495 (4) and 2.485 (4) Å, respectively] to C13 and C11 [2.535 (4) and 2.537 (4) Å, respectively] and C12 [2.560 (4) Å]. The three bond angles around O113 add up to 359.9°, while those around O153 sum to only 354.6°. These trigonal surroundings are a result of extensive donation of π electrons from the O atom to the zirconium centre. π donation from O113 seems slightly more effective than that from O153 and this is corroborated by the respective Zr—O bond lengths of 2.298 (3) and 2.342 (3) Å. These values are comparable to other *trans*-Cl-positioned Zr—O(ether) bond lengths, *e.g.* 2.26 (1) Å in *mer*-[$ZrCl_3(\eta^5$-Cp)(dimethoxyethane)] (Wells *et al.*, 1981), 2.314 (3) Å in *cis,mer*-[$ZrCl_3(\eta^5$-Cp)(thf)$_2$] (Erker *et al.*, 1990) and 2.264 (4) Å in [$ZrCl_2(\eta^5{:}\eta^1$-$C_5H_4CH_2CH_2OMe)(\mu$-Cl)]$_2$ (van der Zeijden *et al.*, 1997).

The Zr—Cl distances [2.4591 (12) and 2.4805 (12) Å] *trans* to oxygen are shorter than those *trans* to Cp [2.5168 (12) Å]. The latter distance is very similar to that in *trans,mer*-[$ZrCl_3\{\eta^5$-$C_5H_3(SiMe_2CH_2P^iPr_2)_2$-1,3}] [2.529 (1) Å; Fryzuk *et al.*, 1995]. Together with our complex, this is a rare example of a pseudo-octahedral mono-Cp zirconium complex having a *trans*-Cp-positioned chloride that is not involved in Zr—Cl—Zr bridging. Accordingly, the other known *trans*-Cp-positioned Zr—Cl distances are much longer, *e.g.* 2.728 (3) Å in [$ZrCl_3(\eta^5$-Cp)]$_n$ (Engelhardt *et al.*, 1984), 2.727 (1) Å in [$ZrCl_2(\eta^5$-Cp){EtC(O)Me}-(μ-Cl)]$_2$ (Erker, 1990), 2.726 (1) Å in [$ZrCl_2(\eta^5$-Cp){EtOC(O)Me}(μ-Cl)]$_2$ (Erker, 1990), 2.684 (6) Å in [$ZrCl_2(\eta^5{:}\eta^1$-$C_5Me_4C_9H_6N)(\mu$-Cl)]$_2$ (Enders *et al.*, 1996) and 2.642 (2) Å in [$ZrCl_2(\eta^5{:}\eta^1$-$C_5H_4CH_2CH_2$-OMe)(μ-Cl)]$_2$ (van der Zeijden *et al.*, 1997).

The ^{1}H NMR spectrum of (I) in solution (see *Experimental*) is in accord with the presence of a mirror plane running through the molecule. The mirror plane can be thought of as running through atoms C13, Zr and Cl13, and bisecting O113 and O153, as well as Cl11 and Cl12. In the crystal, the Cp ring is rotated by about 15° around the Cp—Zr axis away from the symmetric situation, and the molecule is chiral. As a consequence, both of the ether side chains are twisted in the same direction around the Zr—O axes. Therefore, the angle between the Cp plane and the trigonal planes around O113 and O153 is about 53° for both. In solution, the Cp ring obviously twists back and forth 30° around the Cp—Zr axis, while the two ether handles are dragged along in a windscreen wiper fashion.

In the crystal packing, no intermolecular contacts are shorter than normal van der Waals separations.

Experimental

The title compound was obtained as a by-product (*ca* 1–2% yield) during the synthesis of [$ZrCl_2\{\eta^5{:}\eta^1$-$C_5H_4CH_2$-$CH_2OMe)(\mu$-Cl)}]$_2$ (van der Zeijden *et al.*, 1997), probably because of the presence of traces of disubstituted Cp ligand in the $C_5H_5CH_2CH_2OMe$ used (Rees & Dippel, 1992). Orange crystals were obtained from dichloromethane. Calculated mass for $C_{11}H_{17}O_2Cl_3Zr$: 378.8. Mass spectrum (EI; *m/z*): 376/378/380 (M^+), 341/343/345 ([$M-$Cl]$^+$), 317/319/321 ([$M-CH_2CH_2OMe]^+$), 282/284/286 ([$M-$Cl-$CH_2CH_2OMe]^+$). ^{1}H NMR ($CDCl_3$): δ 6.56 (2H, *d*, 2.5 Hz, C_5H_3), 6.50 (1H, *t*, 2.5 Hz, C_5H_3), 3.54 (6H, *s*, OCH_3), 2.80/3.03 (2 × 1H, CpCHH′, *dt*, 14.5 × 6.6 Hz), 3.88/3.98 (2 × 1H, OCHH′, *dt*, 8.5 × 6.6 Hz).

Crystal data

[$ZrCl_3(C_{11}H_{17}O_2)$]
$M_r = 378.82$
Triclinic
$P\bar{1}$
$a = 7.949$ (1) Å
$b = 13.383$ (3) Å
$c = 14.340$ (4) Å
$\alpha = 104.06$ (2)°
$\beta = 102.15$ (2)°
$\gamma = 95.93$ (2)°
$V = 1427.3$ (5) Å^3
$Z = 4$
$D_x = 1.763$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18.46$–21.04°
$\mu = 1.319$ mm^{-1}
$T = 223$ (2) K
Block
0.35 × 0.30 × 0.15 mm
Light brown

Data collection

Enraf–Nonius MACH3 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan data (*MolEN*; Fair, 1990)
$T_{min} = 0.724$, $T_{max} = 0.820$
6200 measured reflections
5764 independent reflections
4750 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 26.29°$
$h = 0 \rightarrow 9$
$k = -16 \rightarrow 16$
$l = -17 \rightarrow 17$
3 standard reflections every 250 reflections frequency: 120 min intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.165$
$S = 1.189$
5680 reflections
311 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 3.4519P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.885$ e Å^{-3}
$\Delta\rho_{min} = -1.335$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Zr1—O113	2.298 (3)	Zr1—C12	2.560 (4)
Zr1—O153	2.342 (3)	C11—C111	1.499 (6)
Zr1—Cl11	2.4591 (12)	C15—C151	1.497 (6)
Zr1—Cl12	2.4805 (12)	C111—C112	1.496 (7)
Zr1—C15	2.485 (4)	C112—O113	1.460 (6)
Zr1—C14	2.495 (4)	O113—C114	1.427 (6)
Zr1—Cl13	2.5168 (12)	C151—C152	1.487 (7)
Zr1—C13	2.535 (4)	C152—O153	1.463 (5)
Zr1—C11	2.537 (4)	O153—C154	1.449 (6)
O113—Zr1—O153	81.33 (12)	C112—C111—C11	109.7 (4)
O113—Zr1—Cl11	160.43 (9)	O113—C112—C111	107.6 (4)
O153—Zr1—Cl11	86.95 (8)	C114—O113—C112	114.2 (4)

O113—Zr1—Cl12	89.66 (9)	C114—O113—Zr1	129.1 (3)
O153—Zr1—Cl12	161.53 (8)	C112—O113—Zr1	116.6 (3)
Cl11—Zr1—Cl12	96.88 (4)	C152—C151—C15	109.7 (4)
O113—Zr1—Cl13	79.22 (8)	O153—C152—C151	108.9 (4)
O153—Zr1—Cl13	81.63 (8)	C154—O153—C152	108.6 (4)
Cl11—Zr1—Cl13	83.62 (4)	C154—O153—Zr1	124.2 (3)
Cl12—Zr1—Cl13	80.87 (5)	C152—O153—Zr1	121.8 (3)

H atoms were calculated and refined as riding atoms with $U_{\rm iso} = 1.2(\text{or } 1.5)U_{\rm eq}(\text{host})$

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *DIAMOND* (Brandenburg, 1996). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1264). Services for accessing these data are described at the back of the journal.

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An Exact Quasi-Ferrodistortive Ordering in (*N*,*N*′-Di-*n*-butylthiourea-*S*)(*N*-salicylideneglycinato-*O*,*N*,*O*′)copper(II)

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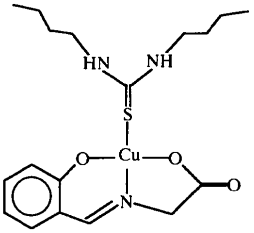
Abstract

The Cu^{II} atom in the title compound, [$Cu(C_9H_7NO_3)$-($C_9H_{20}N_2S$)], adopts distorted square-planar coordination, with a tridentate *N*-salicylideneglycinato Schiff base dianion and an *N*,*N*′-dibutylthiourea ligand bonded *via* its S atom. The molecules stack along [001] and are ordered quasi-ferrodistortively with two different magnetic orientations.

Comment

Owing to the diversity of the resulting structures, copper(II) complexes with tridentate Schiff base dianions of the *N*-salicylideneaminoacidato type (TSB^{2-}) represent suitable models for the elucidation of structural and spectroscopic correlations. We are interested in the behaviour of the EPR (electron paramagnetic resonance) signal of Jahn–Teller-distorted ions with respect to the local geometry and the dipolar interaction between differently oriented polyhedra or molecular axes. For an unambiguous interpretation of EPR results, X-ray structure determinations of a series of substances were undertaken, including that of the title compound, (I).



(I)

Recently, the monomeric structure of (pyrazine)(*N*-salicylidene-α-amino-2-methylpropanato)copper(II) was reported (Warda, 1997, and references therein), for which the quasi-ferrodistortive ordering and the coupled **g** tensor were discussed. The copper(II) layers are stacked parallel and the molecular axes are tilted with