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Tetrachlorobis(tetrahydrofuran-*O*)-zirconium(IV)

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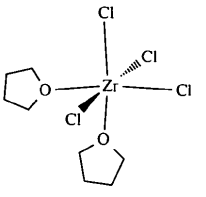
Abstract

The title compound, [$ZrCl_4(C_4H_8O)_2$], contains zirconium with distorted octahedral coordination geometry, with two tetrahydrofuran ligands *cis* with respect to each other. The difference in *trans* influence of the tetrahydrofuran and chloride ligands leads to two marginally different groups of chloride ligands, with Zr—Cl bond lengths of 2.389 (11)/2.398(8) and 2.422 (8)/2.425(8) Å.

Comment

The X-ray crystal structure of the title compound, (I), was determined for comparison with the data of an EXAFS investigation in tetrahydrofuran solution (Bökman & Bertagnolli, 1994). $ZrCl_4$ is of potential interest as its complexes with Lewis bases are effective Ziegler–Natta catalysts soluble in non-polar solvents (Young, 1988).



(I)

The solid-state structure of the title complex exhibits isolated monomeric [$ZrCl_4(thf)_2$] units, with zirconium in a distorted octahedral coordination environment. Within experimental error, the Zr—O distances of both the tetrahydrofuran rings [2.23 (1) and 2.24 (1) Å] are similar to the distance found in solution [2.22 (8) Å].

The chloride ligands *trans* to a tetrahydrofuran ligand show shorter Zr—Cl distances [Zr—Cl1 2.389 (11) and Zr—Cl2 2.398 (8) Å] than the two adjacent *cis*-Cl—Zr linkages [Zr—Cl3 2.422 (8) and Zr—Cl4 2.425 (8) Å]. Though these differences are statistically of marginal significance, they are probably real as a similar *trans* influence has been reported for the crystal structure of [$ZrCl_4$(pinacolone)$_2$] (Galeffi, Simard & Wuest, 1990). The Zr—Cl bond lengths *trans* to pinacolone are, with an average value of 2.391 (5) Å, slightly shorter than the average [2.42 (2) Å] for the *cis*-Cl—Zr bonds. Furthermore, the isostructural complex [$HfCl_4(thf)_2$] gives the same trend for *M*—Cl distances. The mean value of 2.370 (7) Å for the *cis*-Cl—Hf bonds is marginally shorter than the average *trans*-Cl—Hf distance [2.395 (7) Å; Duraj, Towns, Baker & Schupp, 1990].

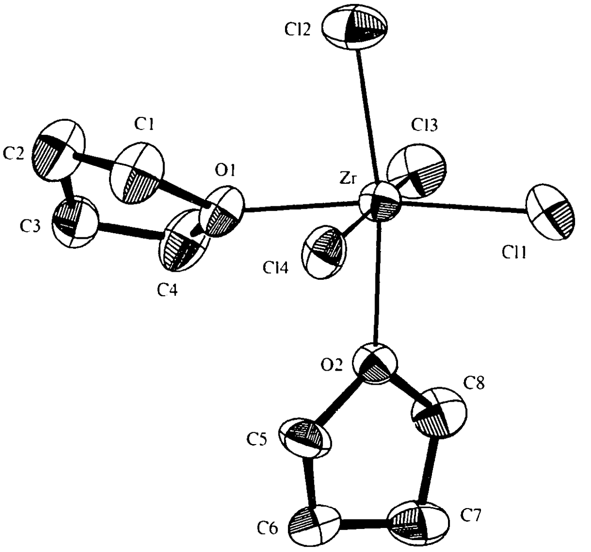


Fig. 1. *ORTEP*II view (Johnson, 1976) of [$ZrCl_4(thf)_2$] showing the labelling of atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted.

The EXAFS molecular structure of the adduct [$ZrCl_4(thf)_2$] in solution (Bökman & Bertagnolli, 1994) is obviously similar to the solid-state molecular structure. The main effect upon dissolving the complex in tetrahydrofuran seems to be an increase of the *cis*-Cl—Zr distance by 0.07 (2) Å, whereas the Zr—O and *trans*-Cl—Zr bonds are not affected within experimental error. A comparison with the crystal structure of the related compound [$ZrCpCl_3(thf)_2$], where Cp is cyclopentadienyl, shows that all distances are larger in the latter [up to 0.12 Å for the average Zr—O bond; *trans*-Cl—Zr 2.468 (1) Å, *cis*-Cl—Zr 2.492 (1) and 2.511 (1) Å; Erker *et al.*, 1990]. It has been suggested, however, that the crystal structure of the trichloride complex exhibits considerable steric strain because of the Cp ligand. In solution, EXAFS experiments show that the bulky Cp ligand is less tightly bonded [2.56 (3) Å] than in the solid state, allowing the other ligands to approach closer to the Zr ion (Bökman & Bertagnolli, 1994). The resultant Zr—Cl distance is 2.44 (1) Å {equal to the average Zr—Cl bond in [$ZrCl_4(thf)_2$]} and no distinction in *cis*- and *trans*-Cl—Zr linkages can be made.

The octahedral coordination of the central Zr ion in [$ZrCl_4(thf)_2$] is distorted as all the Cl—Zr—Cl angles are greater than 90°. The Zr—Cl bonds (except for Zr—Cl1) are noticeably bent towards the thf ligands [angles Cl2—Zr—O2 170.1 (2), Cl3—Zr—Cl4 170.4 (2) and Cl1—Zr—O1 172.3 (2)°]. Steric strain induced by the Cp ligand is responsible for even greater deviations from octahedral coordination in [$ZrCpCl_3(thf)_2$], *e.g.* the angle between the two *cis* chloride ligands is 154.7 (1)°. Since no bond angles were determined in the EXAFS experiment, we cannot comment on any distortion of octahedral coordination for the Zr ion in solution.

Experimental

The title compound was prepared from zirconium tetrachloride and tetrahydrofuran in anhydrous dichloromethane (Manzer, 1982). An air-sensitive crystal was mounted in a 0.50 mm capillary.

Crystal data

[$ZrCl_4(C_4H_8O)_2$]
$M_r = 377.23$
Orthorhombic
$P2_12_12_1$
$a = 14.428 (6)$ Å
$b = 12.885 (6)$ Å
$c = 7.999 (5)$ Å
$V = 1487.1 (13)$ Å^3
$Z = 4$
$D_x = 1.685$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71070$ Å
Cell parameters from 25 reflections
$\theta = 5$–$21°$
$\mu = 1.44$ mm^{-1}
$T = 293 (2)$ K
Plate
0.65 × 0.47 × 0.40 mm
Colourless

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1971 measured reflections
1971 independent reflections
1686 observed reflections [$I > 2\sigma(I)$]

$\theta_{max} = 27.5°$
$h = -20 \rightarrow 0$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 11$
3 standard reflections monitored every 450 reflections
intensity decay: 25.6%

Refinement

Refinement on F^2
$R(F) = 0.0686$
$wR(F^2) = 0.1965$
$S = 1.096$
1969 reflections
137 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1085P)^2 + 2.3194P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 1.906$ e Å^{-3}
$\Delta\rho_{min} = -0.467$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = −0.15 (24)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zr1	0.65451 (6)	0.73782 (7)	0.15978 (12)	0.0506 (3)
Cl1	0.5707 (3)	0.6933 (3)	0.4072 (4)	0.0861 (10)
Cl2	0.7521 (3)	0.8701 (3)	0.2756 (6)	0.0953 (12)
Cl3	0.7662 (2)	0.6006 (2)	0.2072 (6)	0.0878 (11)
Cl4	0.5412 (2)	0.8638 (2)	0.0652 (4)	0.0706 (8)
O1	0.7244 (5)	0.7605 (5)	−0.0872 (10)	0.061 (2)
O2	0.5736 (5)	0.6236 (5)	0.0099 (9)	0.057 (2)
C1	0.7404 (11)	0.8613 (9)	−0.1667 (21)	0.084 (4)
C2	0.8217 (12)	0.8483 (11)	−0.2733 (22)	0.096 (5)
C3	0.8196 (11)	0.7384 (10)	−0.3235 (17)	0.085 (4)
C4	0.7762 (11)	0.6811 (10)	−0.1821 (22)	0.094 (5)
C5	0.5216 (10)	0.6452 (10)	−0.1466 (16)	0.076 (3)
C6	0.5014 (10)	0.5422 (11)	−0.2171 (19)	0.084 (4)
C7	0.4932 (10)	0.4712 (10)	−0.0710 (20)	0.092 (4)
C8	0.5644 (10)	0.5130 (8)	0.0496 (19)	0.079 (3)

Table 2. *Selected geometric parameters (Å, °)*

Zr1—O2	2.229 (10)	O2—C8	1.465 (13)
Zr1—O1	2.237 (13)	O2—C5	1.49 (2)
Zr1—Cl1	2.389 (11)	C1—C2	1.46 (2)
Zr1—Cl2	2.398 (8)	C2—C3	1.47 (2)
Zr1—Cl3	2.422 (8)	C3—C4	1.49 (2)
Zr1—Cl4	2.425 (8)	C5—C6	1.47 (2)
O1—C1	1.464 (14)	C6—C7	1.49 (2)
O1—C4	1.477 (15)	C7—C8	1.51 (2)
O2—Zr1—O1	81.2 (4)	Cl1—Zr1—Cl3	91.8 (3)
O2—Zr1—Cl1	91.3 (4)	Cl2—Zr1—Cl3	93.9 (4)
O1—Zr1—Cl1	172.3 (2)	O2—Zr1—Cl4	85.5 (4)
O2—Zr1—Cl2	170.1 (2)	O1—Zr1—Cl4	86.6 (3)
O1—Zr1—Cl2	89.1 (4)	Cl1—Zr1—Cl4	94.5 (3)
Cl1—Zr1—Cl2	98.5 (4)	Cl2—Zr1—Cl4	92.3 (4)
O2—Zr1—Cl3	87.2 (4)	Cl3—Zr1—Cl4	170.42 (15)
O1—Zr1—Cl3	86.2 (3)		

Data collection: Philips PW1100 software. Cell refinement: Philips PW1100 software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1019). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrakis[μ-(3-bromobenzoato)-μ-(2-dimethylaminoethanolato)-copper(II)]

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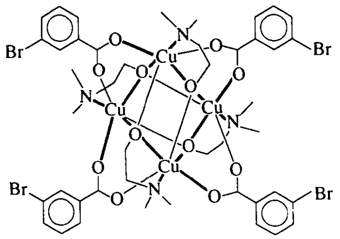
Abstract

A cubane-type Cu_4O_4 core has been found in the title tetrameric copper(II) complex {tetrakis(μ-3-bromobenzoato)-1κO:2$\kappa O'$;2κO:3$\kappa O'$;3κO:4$\kappa O'$;-4κO:1$\kappa O'$-tetrakis[μ-2-(dimethylamino)ethanolato]-1κN,1:2:3$\kappa^3 O$;2κN,2:3:4$\kappa^3 O$;3κN,3:4:1$\kappa^3 O$;4κN,4:1:2$\kappa^3 O$-tetracopper(II), $[Cu_4(C_7H_4BrO_2)_4(C_4H_{10}NO)_4]$}. The short Cu—O$_{\text{ethanolato}}$ bonds form an eight-membered ring folded in a boat-like conformation. The Cu···Cu distances vary between 3.121 (2) and 3.796 (3) Å. Each Cu atom has a distorted octahedral environment. Two ethanolato O atoms, a carboxy O atom and an amino N atom form the equatorial coordination plane, with Cu—O bond lengths in the range 1.914 (12)–1.954 (14) Å and Cu—N bond lengths in the range 2.011 (12)–2.057 (13) Å. The axial sites are occupied by an ethanolato O atom and an O atom of the carboxylate group, with Cu—O distances in the range 2.443 (8)–2.877 (9) Å.

Comment

Monomeric, dimeric, tetrameric, hexameric and nonameric complexes have been obtained from the reactions between 2-dimethylaminoethanol and Cu^{II} carboxylates (Turpeinen, Hämäläinen & Ahlgrén, 1980, 1985; Turpeinen, Hämäläinen & Reedijk, 1987, 1988). It has been found that when copper(II) 4-bromobenzoate reacts with 2-dimethylaminoethanol, a centrosymmetric structure is formed which is composed of three dimers. The dimers are bridged into a hexametallic unit by carboxylate O atoms, with Cu···Cu separations of 2.896 (2) and 2.988 (2) Å (Turpeinen, Hämäläinen & Reedijk, 1988).

The title structure, (I), consists of discrete cubane-like tetrameric molecules which are built up of four $[Cu(BrC_6H_4COO)(Me_2NCH_2CH_2O)]$ units joined together by the ethanolato O atom and carboxylate bridges. Within the Cu_4O_4 core, the long Cu···Cu distances are 3.794 (3) and 3.796 (3) Å, and the four short Cu···Cu distances vary from 3.121 (2) to 3.222 (3) Å.



(I)

The coordination geometry around the Cu atoms is distorted octahedral (4+2). The four equatorial bonds are directed towards two ethanolato O atoms, an amino N atom and a carboxy O atom, with mean values of 1.93, 2.04 and 1.94 Å, respectively. The axial bonds are directed towards an ethanolato O atom and a carboxy O atom, with mean values of 2.75 and 2.60 Å, respectively. The molecular symmetry of the present complex, C_1, has also been found in the related complex $[Cu(Me_2NCH_2CH_2O)(F_3CCOO)]_4$ (Ahlgrén, Turpeinen & Hämäläinen, 1982). The symmetry of the

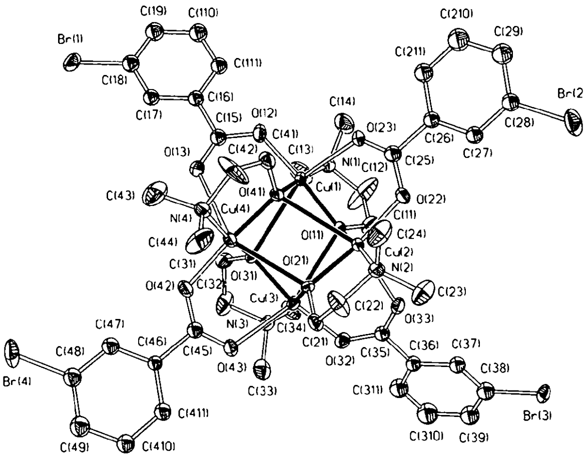


Fig. 1. A view of the title structure (*SHELXTL/PC*; Sheldrick, 1990). Displacement ellipsoids are drawn at the 20% probability level.

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