METAL-ORGANIC COMPOUNDS

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Potassium Hydrogen *cis*-4-Cyclohexene-1,2-dicarboxylate Monohydrate

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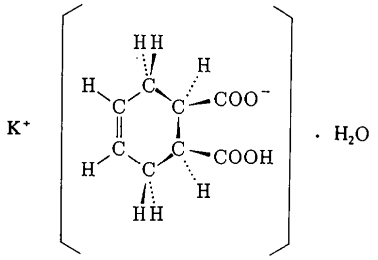
Abstract

The anions of the title compound, $K^+.C_8H_9O_4^-.H_2O$, are linked by intermolecular hydrogen bonds [O···O 2.536 (3) Å] forming chains parallel to the [010] direction of the *Pbca* space group. The K^+ ion is coordinated by eight O atoms. The coordination polyhedron is a distorted cube.

Comment

Dicarboxylic acids with adjacent carboxylic groups and their acid salts in few cases form intramolecular hydrogen bonds; those that do often display extraordinarily short O···O distances (Jessen & Küppers, 1991). *cis*-4-Cyclohexene-1,2-dicarboxylic acid (CCDA) forms intermolecular hydrogen bonds (Küppers & Kim, 1993). Since the formation of the intramolecular hydrogen bond is facilitated by an ionized COO^- group (Küppers & Jessen, 1993), the structure of an acid salt of CCDA was determined in order to check whether the hydrogen *cis*-4-cyclohexene-1,2-dicarboxylate anion yields a further example of a short intramolecular hydrogen bond.



(I)

Crystals were grown from aqueous solutions with a potassium content exceeding the stoichiometric requirement by 50%. The predominating forms of the grown crystals are the orthorhombic dipyramids {112} and {111}, which are capped by the pinacoid {001}. Sometimes small faces {102} are observed.

The displacement ellipsoids and the atom-numbering scheme of the anion are shown in Fig. 1. The ring has a half-chair conformation. The hydrogen *cis*-4-cyclohexene-1,2-dicarboxylate ion does not form an intramolecular hydrogen bond. Instead, the anions are connected by intermolecular hydrogen bonds [O1—H7···O4^{i} 2.536 (3) Å; symmetry code: (i) $\frac{1}{2}-x, y-\frac{1}{2}, z$] forming infinite chains parallel to the [010] direction. The packing is characterized by a sandwich structure with the layers oriented parallel to the (001) plane (Fig. 2). This arrangement is very similar to that in lithium hydrogen *cis*-4-cyclohexene-1,2-dicarboxylate dihydrate

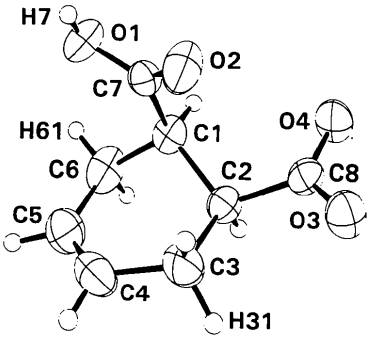


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the anion showing displacement ellipsoids at the 50% probability level. H atoms have fixed radii.

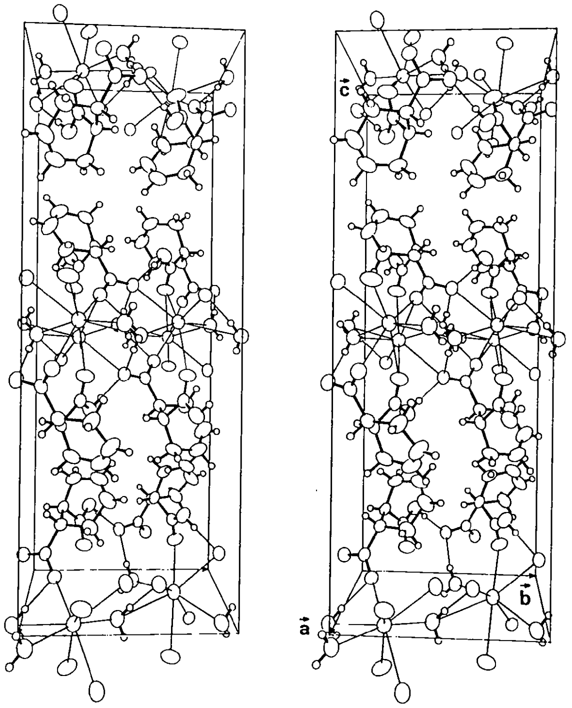


Fig. 2. Stereoscopic view of the crystal structure of the title compound along the *a* axis.

(Kim & Küppers, 1994). The anions orientate their carboxylic groups towards the K/H_2O layers, and their back sides are held together by van der Waals forces. Owing to the weakness of these bonds, the crystals exhibit perfect cleavage along the (001) plane.

The coordination number of the K^+ ion is 8 and the coordination polyhedron is a distorted cube formed by three O atoms of the water molecules and by five O atoms of the carboxylic groups of the anions. The K—O distances range between 2.721 and 3.222 Å; the distance to the next non-coordinated O atom is 3.679 Å.

The water molecule forms two hydrogen bonds to O atoms of the carboxylic groups; one is of medium strength [$W\cdots O3^{ii}$ 2.764 (3) Å; symmetry code: (ii) $-\frac{1}{2}-x, y-\frac{1}{2}, z$] and the other is very weak [$OW\cdots O4^{iii}$ 3.111 (3) Å; symmetry code: (iii) $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$].

Experimental

Crystals of the title compound were formed by slow evaporation of aqueous solution at 293 K.

Crystal data

$K^+.C_8H_9O_4^-.H_2O$
$M_r = 226.27$
Orthorhombic
Pbca
$a = 7.9463\,(15)$ Å
$b = 9.549\,(5)$ Å
$c = 26.364\,(6)$ Å
$V = 2000.5\,(12)$ Å^3
$Z = 8$
$D_x = 1.503$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 27 reflections
$\theta = 6\text{–}20°$
$\mu = 0.524$ mm^{-1}
$T = 293\,(2)$ K
Block
0.76 × 0.57 × 0.31 mm
Colourless

Data collection

Stoe Siemens AED-2 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3452 measured reflections
1762 independent reflections
1269 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0497$
$\theta_{max} = 25.00°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -31 \rightarrow 31$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0434$
$wR(F^2) = 0.1121$
$S = 1.081$
1761 reflections
172 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0832P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.578$

$\Delta\rho_{max} = 0.478$ e Å^{-3}
$\Delta\rho_{min} = -0.337$ e Å^{-3}
Extinction correction: $F_c^* = kF_c[1 + (0.001\chi \times F_c^2\lambda^3/\sin 2\theta)]^{-1/4}$
Extinction coefficient: 0.039 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
C1	0.1302 (3)	0.8272 (3)	0.65972 (10)	0.0376 (6)
C2	−0.0552 (3)	0.8309 (3)	0.64289 (10)	0.0380 (6)
C3	−0.1317 (4)	0.6841 (4)	0.64433 (14)	0.0563 (8)
C4	−0.0683 (5)	0.5986 (4)	0.68818 (15)	0.0669 (10)
C5	0.0489 (5)	0.6402 (4)	0.72001 (13)	0.0633 (9)
C6	0.1406 (4)	0.7748 (4)	0.71468 (12)	0.0535 (8)
C7	0.2368 (3)	0.7392 (2)	0.62425 (10)	0.0377 (6)
C8	−0.0850 (3)	0.9057 (3)	0.59219 (10)	0.0356 (6)
O1	0.3751 (3)	0.6920 (2)	0.64441 (9)	0.0527 (6)
O2	0.1974 (3)	0.7160 (3)	0.58068 (7)	0.0605 (6)
O3	−0.1868 (2)	0.8533 (2)	0.56145 (7)	0.0468 (5)
O4	−0.0093 (2)	1.0196 (2)	0.58343 (7)	0.0466 (5)
K	0.03200 (7)	0.74658 (6)	0.48498 (2)	0.0432 (3)
O*W*	−0.2139 (3)	0.5471 (2)	0.49011 (9)	0.0530 (6)

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

C1—C7	1.516 (4)	C7—O2	1.211 (3)
C1—C6	1.535 (4)	C7—O1	1.301 (3)
C1—C2	1.539 (4)	C8—O3	1.249 (3)
C2—C3	1.528 (4)	C8—O4	1.265 (3)
C2—C8	1.534 (4)	O1—H7	0.81 (4)
C3—C4	1.502 (5)	O*W*—H*W*1	0.87 (4)
C4—C5	1.315 (5)	O*W*—H*W*2	0.84 (3)
C5—C6	1.485 (5)		
C7—C1—C6	111.8 (2)	C5—C6—C1	110.2 (3)
C7—C1—C2	111.7 (2)	O2—C7—O1	122.9 (3)
C6—C1—C2	109.3 (2)	O2—C7—C1	122.8 (2)
C3—C2—C8	112.8 (2)	O1—C7—C1	114.3 (2)
C3—C2—C1	110.6 (2)	O3—C8—O4	122.3 (2)
C8—C2—C1	114.2 (2)	O3—C8—C2	118.6 (2)
C4—C3—C2	112.6 (3)	O4—C8—C2	119.1 (2)
C5—C4—C3	124.4 (3)	C7—O1—H7	108 (3)
C4—C5—C6	123.3 (3)	H*W*1—O*W*—H*W*2	103 (4)

Table 3. *Hydrogen-bonding geometry* (Å, °)

$H7\cdots O4^{i}$	1.73 (4)	$HW2\cdots O4^{iii}$	2.35 (3)
$O1\cdots O4^{i}$	2.536 (3)	$OW\cdots O3^{ii}$	2.764 (3)
$HW1\cdots O3^{ii}$	1.89 (4)	$OW\cdots O4^{iii}$	3.111 (3)
$O1—H7\cdots O4^{i}$	179 (4)	$OW—HW2\cdots O4^{iii}$	150 (4)
$OW—HW1\cdots O3^{ii}$	177 (4)		

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, z$; (ii) $-\frac{1}{2}-x, y-\frac{1}{2}, z$; (iii) $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$.

Data reduction: *REDU*4 (Stoe & Cie, 1988). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). 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.

Many thanks are forwarded to Professor Dr H. Küppers for helpful discussions.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1143). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Racemic Dichloro{(*R*,*R*)-3,3′-(dimethylsilanediyl)bis[(1,2,3,3a,7a-η)-4,5,6,7-tetrahydro-1-indenyl]}zirconium

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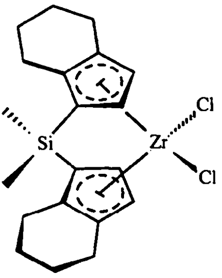
Abstract

The structure of the title compound, $[(CH_3)_2Si(C_9H_{10})_2ZrCl_2]$ has been determined. The coordination geometry about the Zr atom is that of a distorted tetrahedron formed by the two Cl atoms and the centroids of the two silicon-bridged tetrahydroindenyl ligands. The Zr—Cl distances are 2.446 (2) and 2.437 (2) Å, and the Zr—C distances vary from 2.444 (4) to 2.639 (4) Å.

Comment

Chiral complexes of titanium, zirconium and hafnium incorporating two appropriately substituted cyclopentadienyl ligands are finding increasing application in enantioselective synthesis and stereoselective polymerization (Ellis *et al.*, 1993). For practical applications of metallocene-based olefin polymerization catalysts, further improvements in their catalytic activities and in the molar masses of their polyolefin products would be desirable. Previous studies on the activation of complexes of this type by methylaluminoxane (MAO) have shown that increased catalytic activities are associated with the presence of the aromatic six-membered rings in ethylenebis(1-indenyl)zirconium dichloride, as compared with its hydrogenated congener (Stehling *et al.*, 1994). In general, variations in the structures of bridged metallocenes give information on the correlation between metallocene structure and polymerization result, *e.g.* activity of the catalyst, average molar mass and chain microstructure of the polymer (Spaleck *et al.*, 1990; Kaminsky, 1994). We are systematically studying silicon-bridged bis(indenyl) metallocene complexes.



The catalytic properties of both the title complex (Fig. 1) and the non-hydrogenated congener have been discussed (Spaleck *et al.*, 1992). The polar activation in copolymerization of propylene and a phenolic polymer stabilizer when using the hydrogenated congener and MAO was recently reported (Wilén & Näsman, 1994). The crystallographic structure of racemic dichloro{(*R*,*R*)-3,3′-(dimethylsilanediyl)bis[(1,2,3,3a,7a-η)-4,5,6,7-tetrahydro-1-indenyl]}zirconium, (I), has not been reported. In order to compare its structure with other new silane-bridged met-

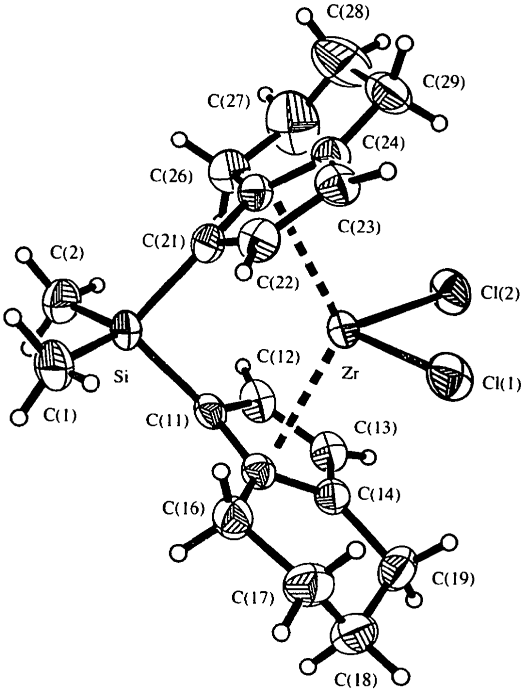


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

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