

C(6)	0.3459 (5)	0.4116 (1)	0.9209 (9)	0.032
C(7)	0.3233 (6)	0.3255 (1)	0.639 (1)	0.045
C(8)	0.4265 (7)	0.2979 (2)	0.777 (2)	0.072
C(9)	0.398 (2)	0.2559 (3)	0.671 (3)	0.173
C(10)	0.317 (1)	0.2611 (2)	0.462 (2)	0.083
C(11)	-0.2373 (4)	0.3964 (1)	1.2395 (8)	0.034
C(12)	-0.3233 (6)	0.3592 (2)	1.327 (1)	0.062

Table 2. Selected geometric parameters (Å, °)

S(1)—C(2)	1.775 (5)	Na(1)···O(7)	2.292 (6)
S(1)—C(3)	1.831 (4)	O(6 ⁱⁱ)···O(2)	2.691 (6)
O(1)—C(6)	1.281 (6)	O(6 ⁱⁱ)···O(4 ⁱⁱⁱ)	2.766 (5)
O(2)—C(6)	1.235 (7)	O(7)···O(1 ^{iv})	2.848 (7)
O(3)—C(5)	1.215 (5)	O(7)···O(3)	2.963 (7)
Na(1)···O(1)	2.304 (4)	O(7)···O(4 ^{iv})	3.160 (7)
Na(1)···O(3)	2.410 (4)	O(8)···O(1 ^{iv})	2.748 (6)
Na(1)···O(3 ⁱ)	2.340 (4)	O(8)···O(6)	2.833 (6)
Na(1)···O(6)	2.305 (4)		
C(2)—S(1)—C(3)	90.7 (2)		

Symmetry codes: (i) $-x, -y + 1, z$; (ii) $-x + 1, -y + 1, z$; (iii) $x + 1, y, z - 1$; (iv) $x, y, z - 1$.

The high values of wR and $(\Delta/\sigma)_{\max}$ result from disorder of the tetrahydrofuryl group, the hydroxyethyl group and the water O atom (O7). Data collection: *AFC-5 Data Collection Software* (Rigaku Corporation, 1984a). Data reduction: *RASA-5P* (Rigaku Corporation, 1984b). Program(s) used to solve structure: *MULTAN11/84* (Main, Germain & Woolfson, 1984). Program(s) used to refine structure: *RASA-5P*. Molecular graphics: *ORTEP* (Johnson, 1965); *PLUTO* (Motherwell & Clegg, 1978).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AS1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Di- μ -chloro-bis[dichlorotris(2-propanol)cerium(III)] at 153 K

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Abstract

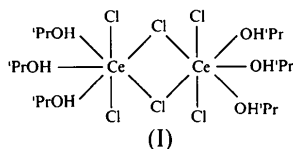
The structure of di- μ -chloro-bis[dichlorotris(2-propanol)cerium(III)], $[\text{CeCl}_3(\text{C}_3\text{H}_8\text{O})_3]_2$, is reported. The Ce atoms are bridged by two Cl atoms and so a dimer is formed.

Comment

The addition of trimethylsilylpropargyl† magnesium bromide to aldehyde affords, predominantly, allenyl alcohol. The regioselectivity changes dramatically when

† Propargyl = 2-propynyl.

cerium organyls are used for the addition and homopropargyl alcohols are formed almost exclusively. These organocerium compounds are prepared from $\text{CeCl}_3 \cdot 4\text{PrOH}$, obtained from the reaction of Ce^{III} chloride with 2-propanol, which forms a dimeric lanthanide chloride–2-propanol complex (Groth & Köhler, 1994). Single crystals were obtained from 2-propanol at room temperature. The molecular structure of the title complex (I) and the atomic numbering scheme are shown in Fig. 1.



The molecule possesses a centre of inversion in the middle of the Ce_2Cl_2 ring. Because of the dimerization the Ce atoms are seven-coordinated. The chloride bridge is asymmetric [Ce1—Cl1 2.980 (3) and Ce1—Cl1ⁱ 2.856 (3) Å; symmetry code: (i) $1-x, 1-y, -z$] and the Ce—Cl distances are longer than the terminal Ce—Cl bonds [Ce1—Cl2 2.799 (2) and Ce1—Cl3 2.727 (3) Å]. Because of steric hindrance the Ce—O distances are also different [Ce1—O1 2.478 (7), Ce1—O2 2.525 (7) and Ce1—O3 2.43 (3) Å]. Two of the 2-propanol groups were found to be disordered. In the O1 group, two positions of each C atom were refined to an occupancy of 0.5:0.5 and then fixed. In the O3 group, two positions of each atom were refined to an occupancy of 0.6:0.4 and then fixed. For this part of the structure, distance restraints, the rigid-bond restraint (Rollet, 1970; Hirshfeld, 1976; Trueblood & Dunitz, 1983) and similarity restraints for the anisotropic displacement parameters were used. Because of the disorder, only the H atom bonded to O2 was found in the difference Fourier map and this was refined with a distance restraint. All other H atoms were included in calculated positions and refined using the riding model.

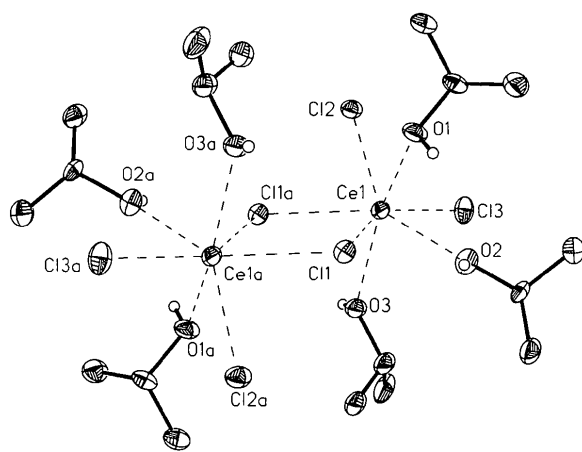


Fig. 1. Structure of the title complex showing 50% probability displacement ellipsoids. The H atoms attached to C atoms are omitted for clarity.

The crystal packing is stabilized by inter- and intramolecular hydrogen-bond interactions involving $\text{O} \cdots \text{H} \cdots \text{Cl}$ interactions between the O1, O2 and O3 atoms, and the Cl3ⁱⁱ and Cl1 atoms [O1 \cdots Cl3ⁱⁱ 3.658 (9), O2 \cdots Cl3ⁱⁱ 3.105 (8) and O3 \cdots Cl1 3.57 (4) Å; symmetry code: (ii) $x-1, y, z$]. All bond distances and angles are comparable with those of the isostructural neodymium compound (Zhongsheng, Shenglong, Fusong, Cheng, Guangdi & Yugu, 1985).

Experimental

Crystal data

$[\text{Ce}_2\text{Cl}_6(\text{C}_3\text{H}_8\text{O})_6]$

$M_r = 853.5$

Triclinic

$P\bar{1}$

$a = 5.904$ (2) Å

$b = 11.181$ (5) Å

$c = 13.354$ (6) Å

$\alpha = 69.04$ (2)°

$\beta = 77.83$ (2)°

$\gamma = 85.99$ (2)°

$V = 804.7$ (6) Å³

$Z = 1$

$D_x = 1.761$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 50 reflections

$\theta = 10\text{--}12.5^\circ$

$\mu = 3.318$ mm⁻¹

$T = 153$ (2) K

Blocks

$0.6 \times 0.3 \times 0.25$ mm

Colourless

Data collection

Stoe Siemens AED four-

circle diffractometer

Profile from $2\theta/\omega$ scans

Absorption correction:

refined from ΔF

$T_{\min} = 0.539$, $T_{\max} = 0.785$

4873 measured reflections

2849 independent reflections

2432 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0373$

$\theta_{\max} = 25.20^\circ$

$h = -6 \rightarrow 7$

$k = -13 \rightarrow 13$

$l = -15 \rightarrow 15$

3 standard reflections

frequency: 90 min

intensity variation: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0561$

$R(F^2) = 0.2053$

$S = 1.151$

2847 reflections

222 parameters

H atoms refined using a riding model

Calculated weights

$w = 1/[\sigma^2(F_o^2) + (0.1116P)^2 + 11.7681P]$

where $P = (F_o^2 + 2F_c^2)/3$

$\Delta\rho_{\max} = 2.471$ e Å⁻³

$\Delta\rho_{\min} = -3.263$ e Å⁻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 (Å²)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ce1	0.65123 (10)	0.44660 (5)	0.16057 (5)	0.0206 (3)
Cl1	0.2359 (5)	0.4314 (2)	0.0718 (2)	0.0244 (6)
Cl2	0.8751 (5)	0.6697 (2)	0.1386 (2)	0.0263 (6)
Cl3	0.8535 (5)	0.3374 (3)	0.3377 (2)	0.0302 (6)

O1	0.3310 (14)	0.5692 (7)	0.2308 (6)	0.027 (2)
C1	0.346 (4)	0.618 (2)	0.3181 (15)	0.027 (3)
C2	0.341 (5)	0.7620 (17)	0.274 (2)	0.029 (4)
C3	0.161 (4)	0.558 (2)	0.4171 (14)	0.031 (3)
C1'	0.267 (4)	0.617 (2)	0.3220 (16)	0.030 (3)
C2'	0.280 (5)	0.7607 (17)	0.279 (2)	0.031 (4)
C3'	0.418 (4)	0.555 (2)	0.4037 (15)	0.030 (3)
O2	0.3774 (13)	0.2729 (7)	0.2972 (6)	0.025 (2)
C4	0.381 (2)	0.1561 (9)	0.3915 (8)	0.022 (2)
C5	0.299 (3)	0.1826 (12)	0.4962 (9)	0.037 (3)
C6	0.242 (2)	0.0528 (10)	0.3835 (10)	0.032 (3)
O3	0.780 (8)	0.273 (2)	0.093 (4)	0.030 (3)
C7	0.726 (4)	0.138 (2)	0.131 (2)	0.035 (3)
C8	0.946 (4)	0.062 (2)	0.131 (2)	0.040 (4)
C9	0.574 (4)	0.114 (2)	0.061 (2)	0.036 (3)
O3'	0.79 (1)	0.272 (3)	0.087 (7)	0.032 (4)
C7'	0.693 (7)	0.142 (3)	0.120 (3)	0.035 (3)
C8'	0.868 (6)	0.047 (3)	0.168 (3)	0.038 (4)
C9'	0.626 (6)	0.125 (4)	0.024 (2)	0.035 (4)

Table 2. Selected geometric parameters (Å, °)

Ce1—O1	2.478 (7)	Ce1—Cl2	2.799 (3)
Ce1—O2	2.525 (7)	Ce1—Cl1 ¹	2.856 (3)
Ce1—O3	2.43 (3)	Ce1—Cl1	2.980 (3)
Ce1—Cl3	2.727 (3)		
O2—Ce1—Cl3	73.6 (2)	O1—Ce1—Cl1 ¹	107.4 (2)
O2—Ce1—Cl2	141.6 (2)	O3—Ce1—Cl3	91.6 (9)
Cl3—Ce1—Cl2	84.30 (9)	O3—Ce1—Cl2	131.6 (11)
O2—Ce1—Cl1 ¹	137.0 (2)	O3—Ce1—Cl1	82.0 (8)
Cl3—Ce1—Cl1 ¹	141.46 (8)	O1—Ce1—Cl3	101.9 (2)
Cl2—Ce1—Cl1 ¹	78.30 (8)	O1—Ce1—Cl2	77.4 (2)
O2—Ce1—Cl1	69.3 (2)	O1—Ce1—Cl1	70.8 (2)
Cl3—Ce1—Cl1	142.88 (8)	O1—Ce1—O2	77.0 (3)
Cl2—Ce1—Cl1	126.68 (8)	O1—Ce1—O3	149.6 (10)
Cl1 ¹ —Ce1—Cl1	72.09 (9)	O2—Ce1—O3	80.9 (12)
O3—Ce1—Cl1 ¹	75.7 (11)	Ce1 ¹ —Cl1—Ce1	107.91 (9)

Symmetry code: (i) 1 - x, 1 - y, -z.

Data collection: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS90* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1081). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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