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Di-*μ*-chloro-bis[heptaaquacerium(III)] tetrachloride

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Key indicators

Single-crystal X-ray study
$T = 120$ K
Mean σ(Ce–O) = 0.003 Å
R factor = 0.030
wR factor = 0.080
Data-to-parameter ratio = 13.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of $[(H_2O)_7CeCl_2Ce(H_2O)_7]Cl_4$, or $[Ce_2Cl_2(H_2O)_{14}]Cl_4$, has been redetermined at 120 K and refined in space group $P\bar{1}$ (No. 2) with a centrosymmetric cation. Refinements in space groups $P\bar{1}$ and $P1$ (No. 1) are discussed.

Comment

The structure of $CeCl_3 \cdot 7H_2O$ has been reported (Peterson *et al.*, 1979) along with the isomorphous La (Habenschuss & Spedding, 1979) and Pr compounds (Habenschuss & Spedding, 1978). These heptahydrates are found only for the early rare earths; the later rare earths form hexahydrates. The La and Pr compounds were refined in space group $P\bar{1}$ (No. 2), whereas the Ce compound was refined in $P1$ (No. 1), this latter decision being heavily influenced by the observation of a piezoelectric effect in the La compound (Bakakin *et al.*, 1974). The structures of $MCl_3 \cdot 7H_2O$ all contain nine-coordinate M derived from seven water molecules and two bridging Cl atoms forming a dimeric 4+ cation. Inspection of the non-H coordinates of the Ce compound clearly shows that those related by the (pseudo) 'centre of symmetry' lie within 3σ for many of the atoms (approximately 2/3 of the 30 non-H x, y, and z pairs).

$$(H_2O)_7Ce \underset{Cl}{\overset{Cl}{\diamond}} Ce(OH_2)_7 \Big]^{4+} \cdot 4Cl^-$$

(I)
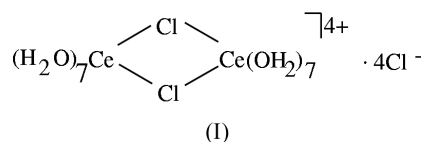
The problem of whether to refine in a centrosymmetric space group or not, as well as identifying the crystal system and Laue group, has been well addressed: '... it simply cannot be determined, by diffraction methods alone, whether a particular structure is centrosymmetric or only approximately so' (Marsh, 1995, 1999). Marsh adopts a pragmatic view in which a centrosymmetric space group should be used if at all possible; only if it is found to be unsatisfactory should the noncentrosymmetric space group be explored, recognizing the well known problems that will probably occur. Warnings against the Hamilton R ratio test (Hamilton, 1965) to resolve the centre of symmetry problem have also been voiced (Baur & Tillmanns, 1986; Marsh, 1995, 1997).

The redetermined structure was solved in space group $P\bar{1}$. Note that the unit cell is a reduced cell (type I with all angles acute). The coordination around Ce is a capped square anti-prism, with O2 as the capping atom (Fig. 1). All the H atoms are involved in either O—H···O [shortest 2.860 (4) Å] or mainly O—H···Cl [shortest 3.034 (3) Å] hydrogen bonding.
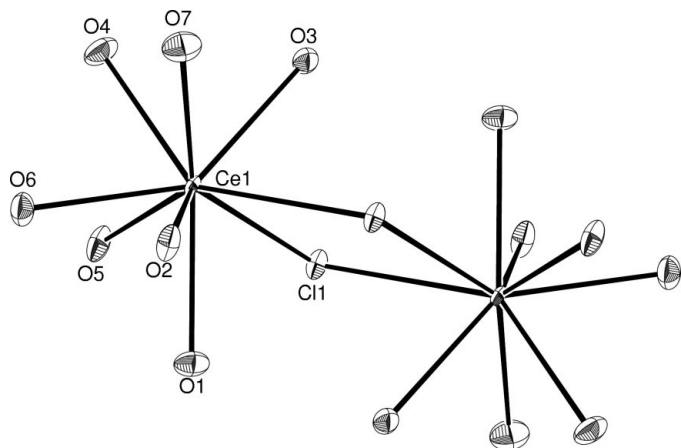
Figure 1
The molecular structure of the $[Ce_2Cl_2(H_2O)_{14}]^{4+}$ cation refined in $P\bar{1}$, showing the atom-labelling scheme. Note that the cation has a centre of symmetry (symmetry operation: $-x$, $-y$, $2-z$). Ellipsoids are drawn at the 70% probability level and H atoms have been omitted for clarity.

Peterson *et al.* (1979) also commented on short H···H contacts.

In the corresponding refinement in the noncentrosymmetric space group $P1$, the s.u. values for Ce—O were *ca* 0.01 Å, with the difference between (pseudo)symmetry-related Ce—O distances ranging from 0.01 (O3/O4) to 0.13 Å (O13/O14) [Peterson *et al.* (1979) atom-labelling scheme]. As noted before (Marsh, 1995), the mean of the pairs of (pseudo)-centrosymmetric bond lengths in $P1$ are close to the single value in $P\bar{1}$. For example, using our data, the mean of Ce1—O1 [2.549 (12) Å] and Ce2—O2 [2.449 (11) Å] in $P1$ is similar to the corresponding Ce1—O6 distance [2.494 (3) Å] in $P\bar{1}$.

Taking the crystallographic data in isolation, it is clear that the refinement in $P\bar{1}$ is more satisfactory, providing as good a fit to the data, without the refinement problems encountered in $P1$.

Experimental

The title compound was prepared fortuitously during attempts to recrystallize $CeCl_3(Ph_3PO)_3$ from hot acetone by slow cooling and allowing the room-temperature solution to evaporate in air.

Crystal data

$[Ce_2Cl_2(H_2O)_{14}]Cl_4$	$Z = 1$
$M_r = 745.16$	$D_x = 2.304$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.9018$ (5) Å	Cell parameters from 5200
$b = 8.2096$ (10) Å	reflections
$c = 9.1877$ (10) Å	$\theta = 2.9$–27.5°
$\alpha = 70.521$ (7)°	$\mu = 4.98$ mm^{-1}
$\beta = 73.142$ (6)°	$T = 120$ (2) K
$\gamma = 81.660$ (5)°	Block, colourless
$V = 536.98$ (10) Å^3	$0.26 \times 0.20 \times 0.20$ mm

Data collection

Nonius KappaCCD area-detector	1879 independent reflections
diffractometer	1849 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.053$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(*SORTAV*; Blessing, 1997)	$h = -9 \rightarrow 9$
$T_{min} = 0.287$, $T_{max} = 0.369$	$k = -9 \rightarrow 9$
7877 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.049P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$+ 0.908P]$
$wR(F^2) = 0.080$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.17$	$(\Delta/\sigma)_{max} = 0.004$
1879 reflections	$\Delta\rho_{max} = 2.28$ e Å^{-3}
144 parameters	$\Delta\rho_{min} = -2.39$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.029 (2)

Table 1
Selected geometric parameters (Å, °).

Ce1—O1	2.520 (3)	Ce1—O6	2.494 (3)
Ce1—O2	2.524 (3)	Ce1—O7	2.505 (3)
Ce1—O3	2.554 (3)	Ce1—Cl1^i	2.8979 (10)
Ce1—O4	2.523 (3)	Ce1—Cl1	2.9264 (10)
Ce1—O5	2.540 (3)		
O6—Ce1—O2	66.65 (10)	O2—Ce1—O3	130.68 (10)
O7—Ce1—O2	70.18 (11)	O2—Ce1—Cl1^i	70.04 (7)
O1—Ce1—O2	67.42 (10)	O2—Ce1—Cl1	128.49 (7)
O4—Ce1—O2	123.90 (10)	Cl1^i—Ce1—Cl1	73.92 (3)
O2—Ce1—O5	124.57 (11)		

Symmetry code: (i) $-x, -y, 2-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···Cl2^i	0.83 (2)	2.36 (3)	3.139 (3)	155 (6)
O1—H1B···Cl2^{ii}	0.83 (2)	2.22 (3)	3.034 (3)	165 (6)
O2—H2A···Cl3^{iii}	0.83 (2)	2.41 (3)	3.196 (3)	159 (6)
O2—H2B···Cl2^{iv}	0.83 (2)	2.35 (3)	3.141 (3)	162 (6)
O3—H3A···Cl3^v	0.84 (2)	2.30 (2)	3.147 (3)	176 (6)
O3—H3B···O1^{vi}	0.83 (2)	2.04 (2)	2.860 (4)	172 (6)
O4—H4A···O3^{vii}	0.84 (2)	2.23 (2)	3.050 (5)	167 (6)
O4—H4B···Cl3^{iv}	0.83 (2)	2.53 (3)	3.315 (3)	157 (6)
O5—H5A···Cl3^{ii}	0.84 (2)	2.50 (4)	3.247 (3)	149 (6)
O5—H5B···Cl2	0.83 (2)	2.53 (3)	3.284 (3)	153 (6)
O6—H6A···Cl3	0.85 (2)	2.30 (3)	3.128 (3)	166 (6)
O6—H6B···O6^{iv}	0.83 (2)	2.489 (12)	2.993 (6)	120.1 (11)
O6—H6B···Cl2	0.83 (2)	2.44 (2)	3.174 (3)	147.7 (10)
O7—H7B···Cl3^v	0.84 (2)	2.43 (2)	3.252 (4)	170 (6)

Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, -y, 1-z$; (iii) $-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $x, y, 1+z$; (vi) $-x, -y, 2-z$; (vii) $1-x, -y, 2-z$.

For the refinement in $P\bar{1}$, a solution readily emerged and a later electron-density map showed plausible positions for all H atoms [d(O—H) = 0.78–1.05 Å] and reasonable H—O—H angles]. H-atom positions were refined with restraints on d(O—H) [target value of 0.84 (2) Å], two anti-bumping restraints to control short H···H contacts (on H6B···H6B' and H4A···H3A'' of 2.0 Å), and a common refined isotropic displacement parameter. Inclusion of an extinction correction led to a modest improvement, giving an $R1$ (all data) value of 0.032.

For the refinement in $P1$, the reflection intensities were transformed to the cell reported by Peterson *et al.* (1979). Refinement proceeded using their published coordinates with anisotropic non-H atoms and fixed H atoms. Problems were experienced with non-positive definite anisotropic displacement parameter values for several O atoms and large correlation coefficients (*ca* 0.90). Convergence was slow, yielding an $R1$ (all data) value of 0.036, but retaining the unsatisfactory anisotropic displacement parameter values.

The maximum and minimum electron-density peaks were located 0.96 and 0.93 Å, respectively, from Ce1.

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Data collection: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

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