

A Refinement of Cerium(III) Trichloride Heptahydrate in Space Group $P1^*$

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Abstract

The crystal and molecular structure of the title compound ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) has been determined from 3143 independent observed reflections collected with the θ - 2θ scan technique and a Syntex $P\bar{1}$ autodiffractometer. The compound crystallizes in the triclinic space group $P1$ with $a = 8.276(3)$, $b = 9.212(2)$, $c = 8.014(2)$ Å, $\alpha = 107.57(2)$, $\beta = 98.39(2)$, $\gamma = 71.51(2)^\circ$, $Z = 2$. The structure was solved by standard heavy-atom methods and refined by a block-diagonal least-squares method to a final R value of 0.0323. Each unit cell consists of the dimeric structural unit $[\text{Ce}_2\text{Cl}_2(\text{OH}_2)_{14}]^{4+}$ and four ionic chlorides. The structure is distinctly noncentrosymmetric and reasons for the lower symmetry are suggested.

Introduction

A useful hydrogen-evolving reaction for inclusion in thermochemical water-splitting cycles is the hydrolysis of cerium(III) chloride oxide to yield cerium(IV) oxide and hydrogen. The various reactions involved are as follows:



In order to elucidate the geometric implications of the various solid phases for the mechanisms of the hydrolysis reactions, and thus give an insight into the

thermodynamics and thermochemistry of the system, the solid-state structures of the various cerium(III) chloride compounds needed to be known. The only structure that has not been unequivocally determined by X-ray diffraction is cerium(III) trichloride heptahydrate. The structure of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ has been determined by Bakakin, Klevstova & Solov'eva (1974) from film data using a centrosymmetric approximation (space group $P\bar{1}$), even though the crystals show a piezoelectric effect indicative of the noncentrosymmetric space group $P1$. The final R factor was 10.7%, no absorption corrections were made, and H positions were not determined. In addition, the authors characterized the coordination polyhedron as a highly distorted tetragonal antiprism with a centered base, which is well above the potential-energy minimum for the tricapped trigonal prism as described by Guggenberger & Muetterties (1976) for ML_9 systems. In a recent review (Drew, 1977), the coordination geometry was re-examined and found to be a very good capped square antiprism. Also, Bakakin *et al.* (1974) do not comment on whether $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ are isomorphous, as was implied by Ivanov (1968) who had incorrectly assigned the unit cell. Thus in order to remedy these inconsistencies and inadequacies in the original structure determination of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, it was deemed necessary to investigate and refine the structure of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ using the appropriate symmetry.

Experimental

Colorless crystals of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (Matheson, Coleman and Bell) were obtained by evaporation of a water solution. A roughly spherical crystal of radius 0.1 mm was placed in a glass capillary which was then sealed to retain the water of hydration. Preliminary photographs verified the lattice parameters and space group ($P1$ or $P\bar{1}$) chosen by Bakakin *et al.* (1974). A refinement of the setting angles obtained on a Syntex $P\bar{1}$ autodiffractometer at 295 K for 15 reflections ($14.5^\circ \leq 2\theta \leq 33.0^\circ$) from this crystal gave the lattice param-

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eters $a = 8.276$ (3), $b = 9.212$ (2), $c = 8.014$ (2) Å, $\alpha = 107.57$ (2), $\beta = 98.39$ (2), $\gamma = 71.51$ (2)° for $Z = 2[\text{CeCl}_3 \cdot 7\text{H}_2\text{O}]$ and $\rho_{\text{calc}} = 2.244$ Mg m⁻³ [$\rho_{\text{obs}} = 2.23$ Mg m⁻³; Bakakin *et al.* (1974)].

3972 reflections were collected with graphite-monochromated Mo $K\alpha$ radiation for $4 \leq 2\theta \leq 60^\circ$ with θ - 2θ scans at 1° min^{-1} over a scan range 0.7° above and below the $K\alpha_1$ - $K\alpha_2$ doublet with background counts for 0.25 of the scan time at each end. A set of six check reflections were examined periodically and showed little variation throughout the data collection. The Lorentz and polarization corrections (Lp) for monochromated radiation (Azaroff, 1955) and the absorption correction (A , $\mu = 4.96 \text{ mm}^{-1}$) for a spherical crystal (Dwiggins, 1975) were applied to the intensities. After merging of duplicates there were 3185 non-zero reflections.

An estimated standard deviation was obtained for each reflection using a modification of the method of McCandlish, Stout & Andrews (1975) where $\sigma(F_o) = [(\sigma_c^2 + p_2 I^2)/4ILpA]^{1/2}$. Counting statistics gave $\sigma_c = R(C + k^2 B)^{1/2}$ where C is the total count in a scan taken at the rate R and k ($= 4$) is the ratio of scan time to the time for the total background count B . The instrument instability constant p ($= 0.0114$) was evaluated from the deviations of the intensities of the check reflections from a smooth curve.

The atomic positions determined by Bakakin *et al.* (1974) and anisotropic thermal parameters were refined in space group $P\bar{1}$ by full-matrix least squares.* The quasi-equivalent positions required for $P\bar{1}$ were generated with two pairs of O atoms displaced from their quasi-equivalent positions as indicated by the apparent thermal motion obtained in the above refinement. The four models thus generated were refined and the one with the lowest residuals was chosen for complete refinement. A final refinement of the model with anisotropic thermal parameters in space group $P\bar{1}$ gave the residuals $R = 0.0348$ and $R_w = 0.0406$ for the 3143 most intense reflections. Successive Fourier syntheses permitted placement of all H atoms. A final refinement of the model with anisotropic non-hydrogen atoms and H-atom positions (280 parameters in three blocks) gave the residuals $R = 0.0323$ and $R_w = 0.0357$. A plot of the normal probability distribution (Abrahams & Keve, 1971) gave a slope (1.174) and an intercept (0.007) indicating that the weights for reflections are slightly overestimated. The data for this refinement included 28 observations for the O-H distance of 1.00 ± 0.1 Å, 14 observations for the H-O-H angle of $105 \pm 5^\circ$ and 28 observations for the Ce-O-H angle of $120 \pm 20^\circ$ (Waser, 1963). The results gave an average O-H distance of 0.94 ± 0.08 Å, an average H-O-H angle of $103 \pm 3^\circ$ and an average Ce-O-H angle of $120 \pm 12^\circ$. Scattering

factors for Ce⁰, Cl¹⁻, O⁰ and H including the anomalous-dispersion corrections for Ce and Cl (*International Tables for X-ray Crystallography*, 1974) were used in this refinement. A similar refinement of the structure with the opposite hand yielded the residuals $R = 0.0335$ and $R_w = 0.0362$ at convergence. A refinement of the structure in space group $P1$ gave the residuals $R = 0.0342$ and $R_w = 0.0381$ for 142 parameters and 35 structural observations of O-H distances, H-O-H angles and Ce-O-H angles. The observed ratio of the weighted residuals (1.0672) is larger than expected (1.0315) for the hypothesis that the structure is centrosymmetric at the 0.005 significance level (Hamilton, 1965). Thus this hypothesis is rejected and the structure is noncentrosymmetric in accord with the positive piezoelectric test observed by Bakakin *et al.* (1974).

Results

The atomic coordinates for the model with the lowest residuals in space group $P\bar{1}$ are given in Tables 1 and 2 along with the estimated standard deviations derived from the least-squares analysis. The perspective view shown in Fig. 1 displays the essential features of the $[\text{Ce}_2\text{Cl}_2(\text{OH}_2)_{14}]^{4+}$ ion. Bond lengths and spherical angles within the ion are systematically recorded in Table 3. A set of coordination-geometry parameters for

Table 1. Fractional coordinates ($\times 10^4$) for $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$

The estimated standard deviations are listed in parentheses.

	x	y	z
Ce(1)*	3121.7 (2)	1736.7 (2)	2164.0 (2)
Ce(2)	-3121.7 (2)	-1736.7 (2)	-2164.0 (2)
Cl(1)	6763 (5)	111 (5)	1503 (5)
Cl(2)	-6752 (6)	-131 (6)	-1465 (7)
Cl(3)	8887 (7)	2176 (7)	6542 (7)
Cl(4)	-8881 (7)	-2177 (7)	-6545 (7)
Cl(5)	2792 (6)	5279 (5)	7915 (6)
Cl(6)	-2808 (6)	-5212 (6)	-7936 (6)
O(1)	1512 (17)	4493 (15)	3987 (16)
O(2)	-1557 (14)	-4422 (11)	-3841 (10)
O(3)	5119 (16)	3005 (15)	4576 (14)
O(4)	-5088 (15)	-2952 (18)	-4474 (18)
O(5)	4162 (16)	3420 (15)	924 (13)
O(6)	-4153 (16)	-3403 (16)	-718 (14)
O(7)	753 (15)	3202 (15)	373 (13)
O(8)	-773 (17)	-3224 (16)	-301 (18)
O(9)	2716 (22)	1534 (20)	5173 (20)
O(10)	-2677 (16)	-1500 (13)	-5119 (14)
O(11)	3855 (19)	-1160 (14)	2117 (16)
O(12)	-3995 (12)	1182 (11)	-2253 (11)
O(13)	398 (14)	999 (12)	2220 (16)
O(14)	-346 (15)	-1220 (15)	-2142 (18)

* From this point all calculations were performed with the CRYSTALS system of computer programs adapted for the Univac 1110 computer (Rollett & Carruthers, 1974).

* The positions of atoms Ce(1) and Ce(2) were refined so that the origin remained exactly halfway between them.

the two nine-coordinate Ce atoms is given in Table 4.* An idealized capped square antiprism indicating the Drew (1977) labeling scheme is shown in Fig. 2.

Discussion

The structure of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ as obtained in this refinement in space group $P1$ is essentially the same as that

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34150 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional coordinates ($\times 10^3$) for hydrogen atoms in $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$

The estimated standard deviations are listed in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
H(11)	138 (18)	478 (13)	512 (11)
H(12)	172 (18)	537 (13)	378 (16)
H(21)	-113 (16)	-546 (13)	-332 (18)
H(22)	-56 (12)	-405 (13)	-359 (17)
H(31)	628 (12)	283 (14)	496 (19)
H(32)	461 (14)	404 (12)	525 (16)
H(41)	-623 (12)	-236 (14)	-468 (16)
H(42)	-479 (16)	-369 (15)	-566 (12)
H(51)	498 (16)	380 (16)	147 (20)
H(52)	345 (14)	413 (14)	44 (17)
H(61)	-469 (16)	-265 (13)	17 (15)
H(62)	-494 (16)	-386 (17)	-129 (18)
H(71)	14 (17)	292 (14)	-64 (15)
H(72)	15 (14)	417 (11)	86 (15)
H(81)	-56 (15)	-251 (15)	-73 (15)
H(82)	31 (11)	-380 (15)	-64 (16)
H(91)	365 (16)	166 (21)	601 (15)
H(92)	188 (15)	127 (21)	582 (17)
H(101)	-351 (14)	-128 (21)	-604 (16)
H(102)	-156 (12)	-162 (21)	-558 (18)
H(111)	273 (12)	-123 (16)	150 (15)
H(112)	466 (14)	-188 (16)	126 (15)
H(121)	-426 (18)	201 (14)	-112 (14)
H(122)	-313 (15)	158 (14)	-259 (17)
H(131)	-78 (11)	158 (16)	189 (19)
H(132)	24 (13)	44 (15)	285 (17)
H(141)	57 (13)	-210 (12)	-254 (18)
H(142)	17 (14)	-56 (14)	-131 (15)

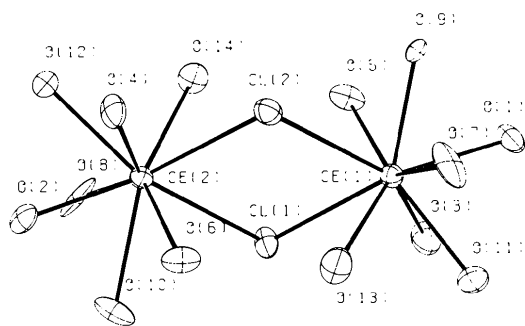


Fig. 1. Perspective view of the dimeric structural unit $[\text{Ce}_2\text{Cl}_2(\text{OH}_2)_{14}]^{4+}$. The numbering scheme for the atoms is defined.

obtained by Bakakin *et al.* (1974) in space group $P\bar{1}$ for $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$. However, the average displacement of the atoms from their quasi-centrosymmetric average positions is 0.048 Å with a maximum displacement of 0.107 Å for O(13) and O(14). Thus, the structure is distinctly noncentrosymmetric.

An examination of the nonbonded contacts between the $[\text{Ce}_2\text{Cl}_2(\text{OH}_2)_{14}]^{4+}$ ions reveals a possible cause for the lower symmetry. The contact distance between pairs of quasi-equivalent O atoms is 3.018 (6) Å for O(1)···O(2), 3.522 (8) Å for O(3)···O(4), 3.311 (7) Å for O(7)···O(8) and 3.554 (9) Å for O(13)···O(14). Because the water molecules are oriented in the structure by their coordination to the Ce atoms, these contacts are not hydrogen bonds but involve close contacts between H atoms on each water molecule across a quasi-inversion center. These are not true inversion centers because they would result in an eclipsed configuration of water molecules with prohibitively short H···H contacts. Thus, a staggered configuration results, destroying the inversion centers and lowering the space-group symmetry to $P1$. Although this structure determination cannot unequivocally determine the H-atom positions, a contact of 1.88 Å was observed for O(1)—H···H—O(2) in the $P1$ refinement. The corresponding contact (1.53 Å) found in the $P\bar{1}$ refinement is much shorter than the van der Waals contact distance for H (Pauling, 1960). It would require a detailed neutron diffraction analysis to unambiguously describe these interactions.

Table 3. Bond distances and spherical angles for the $[\text{Ce}_2\text{Cl}_2(\text{OH}_2)_{14}]^{4+}$ ion

The estimated standard deviations are listed in parentheses.

The spherical polar-coordinate system is defined relative to a Cartesian coordinate system oriented with the capping ligand [O(7) and O(8) on Ce(1) and Ce(2) respectively] on the *x* axis, with the *z* axis bisecting the Cl(1)—Cl(2) vector. The angle θ is that between the *x* axis and the *M*—*L* vector, and ϕ is the angle from the *x* axis to the projection of the *M*—*L* vector on the *xy* plane.

		θ	ϕ
Ce(1)—Cl(1)	2.954 (4) Å	131.00°	22.82°
Ce(1)—Cl(2)	2.895 (5)	70.95	-22.82
Ce(1)—O(1)	2.558 (12)	67.86	152.08
Ce(1)—O(3)	2.601 (11)	125.70	113.59
Ce(1)—O(5)	2.482 (10)	69.39	64.54
Ce(1)—O(7)	2.529 (10)	0.00	0.00
Ce(1)—O(9)	2.551 (14)	123.12	-160.49
Ce(1)—O(11)	2.532 (11)	126.89	-71.23
Ce(1)—O(13)	2.562 (10)	54.97	-116.23
Ce(2)—Cl(2)	2.949 (4)	128.89	-23.04
Ce(2)—Cl(1)	2.916 (4)	69.69	23.04
Ce(2)—O(2)	2.464 (9)	67.00	-151.39
Ce(2)—O(4)	2.520 (12)	125.52	-111.52
Ce(2)—O(6)	2.573 (12)	66.54	-61.87
Ce(2)—O(8)	2.566 (13)	0.00	0.00
Ce(2)—O(10)	2.531 (11)	124.00	159.61
Ce(2)—O(12)	2.574 (5)	130.48	70.56
Ce(2)—O(14)	2.487 (11)	67.70	117.63

Table 4. *Shape parameters for the CeCl₂(OH₂)₇ polyhedra*

The estimated standard deviations are listed in parentheses.

Edge	Type*	<i>d</i>	<i>d</i> _{norm} †	Interior angle‡	δ§	δ _{norm} †
Cl(1)—Cl(2)	<i>l</i>	3.499 (2) Å	1.196 Å	73.5 (1)°	64.42°	51.88°
Cl(1)—O(5)	<i>l</i>	3.247 (12)	1.186	72.8 (3)	52.09	52.37
O(3)—O(5)	<i>l</i>	3.024 (13)	1.189	73.0 (3)	43.74	49.94
O(3)—O(1)	<i>l</i>	2.898 (17)	1.123	68.4 (4)	56.27	54.27
O(9)—O(1)	<i>l</i>	2.982 (21)	1.167	71.4 (5)	50.55	51.49
O(9)—O(13)	<i>l</i>	2.845 (19)	1.113	67.6 (4)	56.95	56.58
O(11)—O(13)	<i>l</i>	2.917 (18)	1.145	69.9 (4)	50.40	55.02
O(11)—Cl(2)	<i>l</i>	3.211 (13)	1.978	72.2 (3)	51.76	54.92
O(7)—Cl(2)	<i>c</i>	3.162 (13)	1.161	71.0 (3)	62.86	59.55
O(7)—O(5)	<i>c</i>	2.852 (17)	1.138	69.4 (4)	51.18	57.15
O(7)—O(1)	<i>c</i>	2.839 (15)	1.116	67.9 (4)	60.96	60.42
O(7)—O(13)	<i>c</i>	2.952 (16)	1.160	70.9 (4)	56.18	61.13
Cl(1)—O(9)	<i>d</i>	4.398 (20)	1.595	105.8 (10)	7.18	1.43
O(3)—O(11)	<i>d</i>	4.133 (20)	1.610	107.3 (8)	-6.78	-1.44
Cl(2)—O(5)	<i>s</i> ₁	3.508 (13)	1.300	81.0 (3)	39.78	41.59
O(5)—O(1)	<i>s</i> ₁	3.247 (17)	1.288	80.2 (4)	36.98	38.43
O(1)—O(13)	<i>s</i> ₁	3.460 (17)	1.351	85.0 (4)	33.78	33.08
O(13)—Cl(2)	<i>s</i> ₁	3.740 (13)	1.368	86.3 (3)	41.12	35.11
Cl(1)—O(3)	<i>s</i> ₂	3.120 (13)	1.118	68.0 (3)	75.01	70.20
O(3)—O(9)	<i>s</i> ₂	2.898 (19)	1.125	68.4 (4)	63.98	67.53
O(9)—O(11)	<i>s</i> ₂	2.927 (21)	1.152	70.3 (5)	60.17	65.18
O(11)—Cl(1)	<i>s</i> ₂	3.144 (14)	1.139	69.4 (3)	66.30	69.21
Cl(1)—Cl(2)	<i>l</i>	3.499 (2)	1.193	73.2 (1)	61.99	51.14
Cl(2)—O(6)	<i>l</i>	3.266 (14)	1.978	72.2 (3)	54.18	52.16
O(4)—O(6)	<i>l</i>	3.115 (18)	1.223	75.4 (4)	43.22	48.28
O(4)—O(2)	<i>l</i>	2.846 (15)	1.142	69.6 (4)	54.42	56.13
O(10)—O(2)	<i>l</i>	2.993 (15)	1.198	73.6 (3)	50.17	50.26
O(10)—O(14)	<i>l</i>	2.843 (16)	1.133	69.0 (4)	56.89	57.14
O(12)—O(14)	<i>l</i>	3.134 (15)	1.238	76.5 (3)	46.30	50.90
O(12)—Cl(1)	<i>l</i>	3.358 (9)	1.219	75.1 (2)	53.65	54.51
O(8)—Cl(1)	<i>c</i>	3.145 (15)	1.143	69.7 (3)	60.97	56.99
O(8)—O(6)	<i>c</i>	2.819 (18)	1.097	66.5 (4)	53.64	56.93
O(8)—O(2)	<i>c</i>	2.778 (16)	1.104	67.0 (4)	58.23	58.13
O(8)—O(14)	<i>c</i>	2.815 (16)	1.114	67.7 (4)	57.56	61.22
Cl(2)—O(10)	<i>d</i>	4.414 (20)	1.608	107.1 (8)	-2.99	-3.06
O(4)—O(12)	<i>d</i>	4.014 (20)	1.576	104.0 (7)	2.73	3.06
Cl(1)—O(6)	<i>s</i> ₁	3.450 (14)	1.253	77.5 (3)	41.74	42.21
O(6)—O(2)	<i>s</i> ₁	3.260 (15)	1.294	80.6 (4)	36.86	37.90
O(2)—O(14)	<i>s</i> ₁	3.258 (15)	1.316	82.3 (4)	33.05	35.62
O(14)—Cl(1)	<i>s</i> ₁	3.712 (14)	1.369	86.4 (3)	41.01	37.53
Cl(2)—O(4)	<i>s</i> ₂	3.062 (14)	1.112	67.6 (3)	74.02	69.96
O(4)—O(10)	<i>s</i> ₂	2.906 (19)	1.151	73.6 (3)	64.80	66.41
O(10)—O(12)	<i>s</i> ₂	2.857 (14)	1.119	68.1 (3)	68.12	69.04
O(12)—Cl(2)	<i>s</i> ₂	3.114 (11)	1.122	68.3 (2)	70.02	69.78

* Labeled according to Drew (1977) for a capped square antiprism. The labeling scheme is indicated in Fig. 2.

† Calculated for the normalized polyhedron with all *M*-*L* distances equal to 1 Å.‡ The *L*-*M*-*L* angle.

§ The interfacial dihedral angle.

A second reason for the lack of a center of symmetry suggests itself from a comparison of the possible hydrogen-bonded contacts given in Table 5. In particular, the intra-ionic contact O(6)···O(11), 2.87 Å, is much shorter than the quasi-centrosymmetrically related contact O(5)···O(12), 3.00 Å. This has the effect of bending the [Ce₂Cl₂(OH₂)₁₄]⁴⁺ complex across the Cl(1)—Cl(2) line. Other similar inequalities can be found with differences between the pairs of quasi-

equivalent contacts ranging from nearly zero to 0.22 Å. It would appear that the structure has been distorted from the centrosymmetric ideal in order to form some shorter hydrogen bonds at the expense of having longer ones (or none at all) at the quasi-equivalent contacts.

The coordination geometry in the [La₂Cl₂(OH₂)₁₄]⁴⁺ ion was described by Bakakin *et al.* (1974) as a 'highly distorted tetragonal antiprism with a centered base'. Drew (1977) pointed out that a consideration of the

Table 5. Possible hydrogen-bonding contacts in $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$

The estimated standard deviations are listed in parentheses.

$\text{Cl}(1) \cdots \text{O}(10)$	3.372 (12) Å	$\text{Cl}(2) \cdots \text{O}(9)$	3.395 (16) Å
$\text{Cl}(1) \cdots \text{O}(13)$	3.290 (11)	$\text{Cl}(2) \cdots \text{O}(14)$	3.353 (12)
$\text{Cl}(3) \cdots \text{O}(2)$	3.141 (12)	$\text{Cl}(4) \cdots \text{O}(1)$	3.133 (15)
$\text{Cl}(3) \cdots \text{O}(3)$	3.251 (12)	$\text{Cl}(4) \cdots \text{O}(4)$	3.300 (13)
$\text{Cl}(3) \cdots \text{O}(7)$	3.240 (11)	$\text{Cl}(4) \cdots \text{O}(8)$	3.205 (15)
$\text{Cl}(3) \cdots \text{O}(9)$	3.321 (17)	$\text{Cl}(4) \cdots \text{O}(10)$	3.308 (13)
$\text{Cl}(3) \cdots \text{O}(12)$	3.170 (11)	$\text{Cl}(4) \cdots \text{O}(11)$	3.133 (15)
$\text{Cl}(3) \cdots \text{O}(14)$	3.440 (11)	$\text{Cl}(4) \cdots \text{O}(13)$	3.219 (10)
$\text{Cl}(5) \cdots \text{O}(1)$	3.113 (13)	$\text{Cl}(6) \cdots \text{O}(2)$	3.227 (9)
$\text{Cl}(5) \cdots \text{O}(3)$	3.289 (13)	$\text{Cl}(6) \cdots \text{O}(4)$	3.337 (15)
$\text{Cl}(5) \cdots \text{O}(5)$	3.240 (10)	$\text{Cl}(6) \cdots \text{O}(6)$	3.055 (12)
$\text{Cl}(5) \cdots \text{O}(6)$	3.067 (13)	$\text{Cl}(6) \cdots \text{O}(5)$	3.058 (13)
$\text{Cl}(5) \cdots \text{O}(8)$	3.179 (14)	$\text{Cl}(6) \cdots \text{O}(7)$	3.146 (13)
$\text{O}(5) \cdots \text{O}(12)$	3.005 (16)	$\text{O}(6) \cdots \text{O}(11)$	2.871 (18)
$\text{O}(9) \cdots \text{O}(12)$	3.159 (19)	$\text{O}(10) \cdots \text{O}(11)$	3.352 (19)

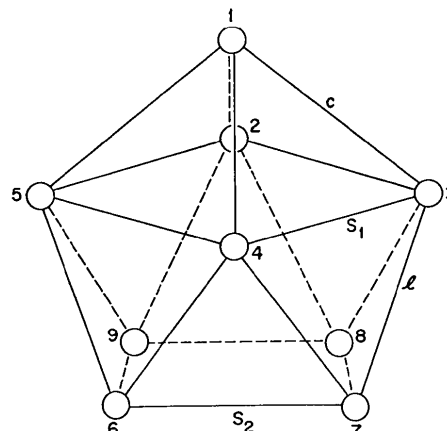


Fig. 2. An idealized capped square antiprism indicating the labeling scheme used in Table 4.

Table 6. Average shape parameters for the $\text{CeCl}_2(\text{OH}_2)_7$ capped square antiprisms

The estimated standard deviations in the averaged values are listed in parentheses.

Edge	Ce(1)		Ce(2)		Ideal Coulombic (Robertson, 1977)	
	\bar{d}_{norm}	$\bar{\delta}_{\text{norm}}$	\bar{d}_{norm}	$\bar{\delta}_{\text{norm}}$	d	δ
4c	1.14 (2) Å	59.6 (17)°	1.11 (2) Å	58.3 (20)°	1.129 Å	58.9°
8l	1.16 (3)	53.3 (22)	1.19 (4)	52.6 (31)	1.183	52.7
4s ₁	1.33 (4)	37.0 (37)	1.31 (5)	38.3 (29)	1.318	38.2
4s ₂	1.13 (2)	68.0 (22)	1.13 (2)	68.8 (16)	1.119	69.1

coordination geometry with normalized $M-L$ bonds shows it to be a nearly perfect example of a capped square antiprism. In the present case, a consideration of the normalized polyhedral shape parameters in Table 4 shows the coordination geometries for the $\text{CeCl}_2(\text{OH}_2)_7$ complexes are also nearly perfect capped square antiprisms. As would be expected for this highly charged ion, the average normalized edge lengths and dihedral angles (Table 6) are virtually identical to those obtained by Robertson (1977) for a Coulombic repulsion between the ligands. In addition, the angles (Table 3) made by the $\text{Ce}-L$ bonds with the unique axis of the polyhedron [$\text{Ce}(1)-\text{O}(7)$ or $\text{Ce}(2)-\text{O}(8)$ respectively] show that the capped face is spread out to accept the capping ligand. Thus the average θ_1 is 66 (5)° as compared with the uncapped face where the average θ_2 is 53 (3)°. The Coulombic-repulsion capped square antiprism has identical values, $\theta_1 = 68.74^\circ$ and $\theta_2 = 52.33^\circ$. The capped and uncapped square faces of the two normalized $\text{CeCl}_2(\text{OH}_2)_7$ polyhedra are flat; the r.m.s. displacements from the planes are less than the e.s.d.'s in the atom positions. These square faces are parallel with interplanar angles of 3.6 and 2.3° for the polyhedra around Ce(1) and Ce(2) respectively.

Finally, the $\text{Ce}-\text{O}$ bonds for the capping water molecules are normal, 86.0–88.5°, to both square faces in each polyhedron.

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