The Crystal Structure of β-$CsReO_4$, the Room-Temperature Modification of Cesium Perrhenate

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The crystal structure of β-$CsReO_4$, the room-temperature modification of cesium perrhenate, was determined from single-crystal X-ray data as orthorhombic, space group Pnma, a = 5.7556(9), b = 5.9964(8), c = 14.310(2) Å and Z = 4.

The structure was refined to R = 0.027, R_w = 0.023 for 779 absorption-corrected reflections. It represents an orthorhombic distortion of the tetragonal high-temperature phase α-$CsReO_4$. The structure of β-$CsReO_4$ comprises isolated ReO_4 tetrahedra, linked together by Cs ions. The average Re–O distance was found to be 1.714(4) Å.

Cesium perrhenate undergoes a reversible phase transition from the room-temperature modification β-$CsReO_4$ to a tetragonal high-temperature modification α-$CsReO_4$ [1, 2]. By means of high-temperature single-crystal X-ray diffraction we recently refined the structure of α-$CsReO_4$ and confirmed the space group to be $I4_1/amd$ [3]. Concerning the crystal structure of the room-temperature modification the space group was proposed to be Pnma and the positional parameters of the heavy atoms have been basically determined [4]. Since the atomic co-ordinates of the oxygen atoms remained unknown we decided to investigate this subject.

Cesium perrhenate was synthesized by neutralization of perrhenic acid with cesium carbonate [3]. The precipitated salt was purified by several recrystallizations from water. Single crystals were obtained by slow evaporation of a saturated aqueous solution of $CsReO_4$ at ambient temperature in air.

A colourless transparent crystal (approx. dimensions 0.1×0.07×0.08 mm) bounded by {112} and {001} crystallographic forms was selected for the X-ray investigations. Data collection was performed on an Enraf-Nonius CAD-4 diffractometer using MoKα radiation (graphite monochromator in incident beam). The unit cell parameters were obtained by least-squares refinement based upon 25 carefully centred reflections in the range $8.3 \leq \theta \leq 13.7°$. Three standard reflections were measured every 100 min, indicating only random fluctuations in intensity. After reduction of the 1614 recorded data a set of 779 independent reflections with $I > 0\sigma(I)$ remained of which all were used in the subsequent calculations. Crystallographic and experimental data are summarized in Table I.

Systematic absences of the type $(0kl)$: $k+l = 2n+1$ and $(hk0)$: $h = 2n+1$ were observed, agreeing with space groups Pnma and $Pn2_1a$. The results of the structure refinement confirmed the centrosymmetric space group Pnma.

All calculations were carried out using the programs SHELX-76 [5] and SHELXS-86 [6]. Atomic scattering factors and corrections for anomalous dispersion were taken from the International Tables for X-ray Crystallography [7].

The structure was solved by Patterson methods, followed by successive difference Fourier synthe-

Table I. Crystal data, data collection and refinement parameters for β-$CsReO_4$[a].

Formula	$CsReO_4$
Molecular weight	383.11 g·mol^{-1}
Space group	Pnma (Nr. 62)
Cell dimensions	a = 5.7556(9) Å
	b = 5.9964(8) Å
	c = 14.310(2) Å
	V = 493.87(9) Å^3
Z	4
Density (calcd)	5.153 g·cm^{-3}
μ(MoKα)	32.0 mm^{-1}
F(000)	648
Temperature	297(1) K
Radiation	MoKα (λ = 0.71073 Å)
Scan mode	$\omega-2\theta$
Scan width	$(0.6 + 0.35 \tan\theta)°$
2θ range	$4° \leq 2\theta \leq 60°$
hkl limits	$-8 \leq h \leq 8; 0 \leq k \leq 8; 0 \leq l \leq 20$
$(\sin\theta/\lambda)_{max}$	0.7 Å^{-1}
Recorded reflections	1614
Unique reflections, R_{int}	779, 0.027
Reflections used in least-squares refinement	779
Parameters refined	36
$(\Delta/\sigma)_{max}$	0.001
Weighting scheme	$w = 0.9014 \cdot \sigma^{-2}(F_o)$
Final R, R_w	0.027, 0.023
$(\Delta\varrho)_{max, min}$	+1.0, −1.1 e·Å^{-3}
Extinction coefficient g	$1.44(1) \cdot 10^{-7}$

[a] Here, as in the following tables, the standard deviations are given in parentheses.

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Table II. Atomic positional parameters and displacement factores [Å^2] for β-$CsReO_4$. Fractional atomic co-ordinates and equivalent isotropic displacement parameters[a].

Atom	x/a	y/b	z/c	U_{eq}
Re	0.03835(6)	1/4	0.37984(2)	0.02191(9)
Cs	0.02497(9)	3/4	0.12698(3)	0.0297(2)
O(1)	0.822(1)	1/4	0.0838(4)	0.038(2)
O(2)	0.856(1)	1/4	0.4737(5)	0.056(3)
O(3)	0.0122(8)	0.5154(8)	0.6859(3)	0.049(2)

Anisotropic displacement factors

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	0.0209(2)	0.0219(2)	0.0229(2)	0	−0.0014(1)	0
Cs	0.0329(3)	0.0292(3)	0.0271(3)	0	0.0067(2)	0
O(1)	0.024(3)	0.038(4)	0.051(3)	0	−0.008(3)	0
O(2)	0.053(4)	0.065(5)	0.050(4)	0	0.028(3)	0
O(3)	0.053(3)	0.039(3)	0.055(3)	0.014(2)	−0.001(2)	0.017(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected interatomic distances [Å] and bond angles [°].

Re−O(1)	1.716(6)	O(1)−Re−O(2)	110.4(3)
−O(2)	1.705(7)	O(1)−Re−O(3)	109.1(2) (2×)
−O(3)	1.717(5) (2×)	O(2)−Re−O(3)	109.1(2) (2×)
		O(3)−Re−O(3)	110.1(2)
Cs−O(2)	3.101(7)	Re−Cs	4.1040(4) (2×)
−O(3)	3.122(5) (2×)	−Cs	4.2107(4) (2×)
−O(1)	3.142(6)	−Cs	4.3387(6)
−O(3)	3.215(5) (2×)	Re−Re	4.5837(3) (2×)
−O(1)	3.275(2) (2×)	Cs−Cs	4.5473(7) (2×)
−O(3)	3.578(5) (2×)		
−O(2)	3.833(4) (2×)		

ses. After isotropic refinement a numerical correction for absorption was applied to the original data set (program DIFABS, [8]). The final full-matrix least-squares refinement (including anisotropic displacement factors and an extinction correction of the form $F_{corr} = F_c(1-gF_c^2/\sin\theta)$) converged at $R = 0.027$ and $R_w = 0.023$. Atomic positions and displacement factors for β-$CsReO_4$ are given in Table II, derived atomic distances and angles in Table III*.

The crystal structure of β-$CsReO_4$ comprises isolated ReO_4 tetrahedra which are linked together by cesium ions. The average Re−O distance was found to be 1.714(4) Å. Cesium is tenfold co-ordinated by oxygen with an average Cs−O distance of 3.262(4) Å. Fig. 1 shows a view of the structure.

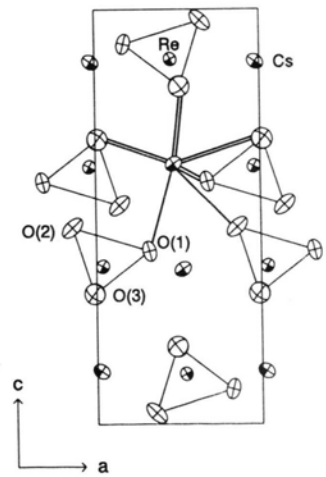

Fig. 1. ORTEP [11] plot of the structure of β-$CsReO_4$. The projection on (010) shows the arrangement of the ReO_4 tetrahedra and the co-ordination of one Cs cation. Thermal ellipsoids are scaled to enclose 50% propability for all atoms.

* Lists of structure factors, bond distances and bond angles have been deposited at the Fachinformationszentrum Karlsruhe GmbH, D-W-7514 Eggenstein-Leopoldshafen 2. Copies may be obtained by quoting the depository number CSD 57083, the name of the authors and literature citation.

The present single-crystal study confirms the space group and the positional parameters of the heavy atoms for β-$CsReO_4$ as proposed by Beintema [4]. β-$CsReO_4$ is isomorphous with $CsTcO_4$ [9] and $RbOsO_3N$ [10]. It represents an orthorhombic distortion of the tetragonal high-temperature modification α-$CsReO_4$ and is topologically related to the scheelite type as well [3].

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[1] B. Kanellakopoulos, J. Inorg. Nucl. Chem. **28,** 813 (1966).
[2] H. Beyer, A. Müller, and B. Krebs, Z. Phys. Chem. **234,** 423 (1967).
[3] K.-J. Range, P. Rögner, A. M. Heyns, and L. C. Prinsloo, Z. Naturforsch. **47b,** 1513 (1992).
[4] J. Beintema, Z. Kristallogr. **97,** 300 (1937).
[5] G. M. Sheldrick, SHELX-76. A program for the solution of crystal structures. Univ. of Cambridge, England (1976).
[6] G. M. Sheldrick, SHELXS-86. A program for crystal structure determination, Universität Göttingen (1986).
[7] International Tables for X-ray Crystallography, Vol. IV; The Kynoch Press, Birmingham (1974).
[8] N. Walker and D. Stuart, Acta Crystallogr. **A39,** 159 (1983).
[9] G. Meyer and R. Hoppe, Z. Anorg. Allg. Chem. **420,** 40 (1976).
[10] P. L'Haridon, R. Pastuszak, and Y. Laurent, J. Solid State Chem. **43,** 29 (1982).
[11] C. K. Johnson, ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee (1965).