TU Clausthal

Synthesis, Crystal Structure and Vibrational Characterization of Cesium Carbonate Triperoxido Hydrate, $Cs_2CO_3 \cdot 3\ H_2O_2$

Introduction

Carbonate peroxido hydrates like $Na_2CO_3 \cdot 1{,}5\ H_2O_2$ [1] are well known as bleaching agents. The oxidizing effect of these so-called “percarbonates” is also used in chemical treatments. In addition to this usage, reactions of percarbonates are ecologically more harmless than those with perborates, which were usually used as bleaching agents in the past.

By variation of the cation it is possible to achieve new alkali metal carbonate peroxido hydrates. In this publication we present the structure of a new cesium carbonate triperoxido hydrate, $Cs_2CO_3 \cdot 3\ H_2O_2$.

Experimental

The title compound was prepared by adding cesium hydrogen carbonate to cold, concentrated hydrogen peroxide (ca 76 % solution). The resulting solution was layered with ethanol (approximately half the volume of the solution) and allowed to stand at -15 °C. After a few days $Cs_2CO_3 \cdot 3\ H_2O_2$ precipitated. Due to the fact, that the obtained product is unstable at room temperature, the structure was verified by X-ray structure analysis and Raman spectroscopy at low temperatures (223 K).

Structure description

Cesium carbonate triperoxido hydrate crystallizes in the orthorhombic space group *Pccn* (No. 56) with eight formula units per unit cell and cell parameters *a* = 5.953(1) Å, *b* = 16.928(2) Å, *c* = 17.851(2) Å and *V* = 1798.8(3) Å (Tab. 1)

The crystal structure consists of three crystallographically different cesium ions, one carbonate group and four hydrogen peroxide molecules, which are involved in a hydrogen bonding network. The corresponding bond lengths and angles are presented in Tab. 2.

In Fig. 1 the crystal structure is shown along [100]. Along b-axis two layers of $[(H_2O_2)(CO_3)^{2-}(H_2O_2)Cs1]$ alternate with one layer of $[(H_2O_2)Cs2(H_2O_2)Cs3]$. Cs1 shows a coordination number of eleven and the other two cesium ions are coordinated by eight oxygen atoms (Tab. 2). In Fig. 2 and 3 the coordination polyhedra of the cesium ions are presented. The Cs1 polyhedra are connected by hydrogen peroxide molecules. The face-sharing Cs2/Cs3 polyhedra are connected by H_2O_2 molecules to adjacent Cs2/Cs3 polyhedra on both sides.

The title compound crystallizes in the same orthorhombic space group as the known rubidium carbonate triperoxido hydrate, $Rb_2CO_3 \cdot 3\ H_2O_2$ [2] and shows similarities in the structural setting.

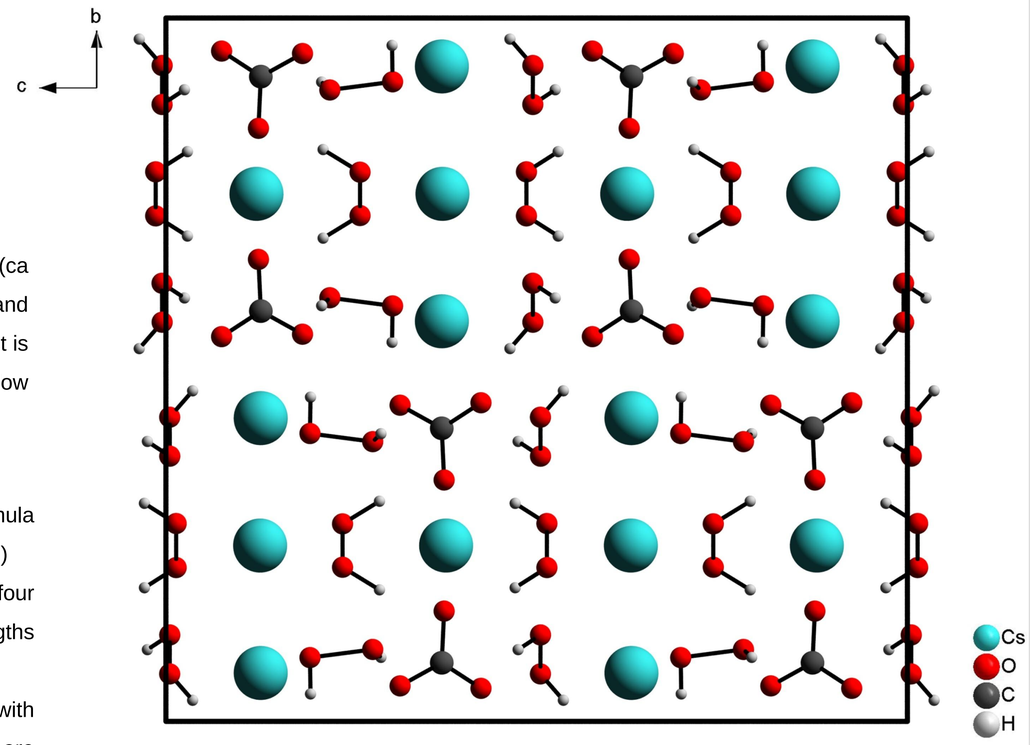

Fig. 1 The structure of $Cs_2CO_3 \cdot 3\ H_2O_2$ with the unit cell shown along [100]

Tab. 1 Crystallographic Data for $Cs_2CO_3 \cdot 3\ H_2O_2$

Crystal system	orthorhombic
Space group / *Z*	*Pccn* (No. 56) / 8
a [Å]	5.953(1)
b [Å]	16.928(2)
c [Å]	17.851(2)
Volume [Å³]	1798.8(3)
D_{calc} [g · cm⁻³]	3.160
Measurement device	STOE IPDS II
μ (MoK_α) [mm⁻¹]	8.124
F(000)	1552
T [K]	223
Crystal size [mm³]	0.10 x 0.20 x 0.20
$\Theta_{min,\ max}$ [°]	2.28 – 25.03
h_{min}, h_{max}, k_{min}, k_{max}, l_{min}, l_{max}	-7, 6, -20, 20, -21, 19
Total number of reflections	1590
Unique reflections	1333
Data / parameters	1590 / 134
Goodness-of-Fit	1.137
R indeces [*I*>2σ(*I*)]	*R*1 = 0.0350 ; *wR*2 = 0.0880
R indeces (all data)	*R*1 = 0.0415 ; *wR*2 = 0.0925
Largest diff. peak and hole [e Å⁻³]	1.81 / -1.38

Tab. 2 Bond lengths [Å] and angles [°] for $Cs_2CO_3 \cdot 3\ H_2O_2$

Coordination of Cesium

Cs1 – O1	3.288(5)	Cs2 – O1	3.279(5)	Cs3 – O2	3.174(5)
Cs1 – O2	3.388(5)	Cs2 – O1^{vii}	3.279(5)	Cs3 – O2^{x}	3.174(5)
Cs1 – O3	3.235(5)	Cs2 – O2^{i}	3.105(5)	Cs3 – O4^{viii}	3.400(4)
Cs1 – O5^{i}	3.308(5)	Cs2 – O2^{v}	3.105(5)	Cs3 – O4^{ix}	3.339(4)
Cs1 – O5^{iv}	3.357(5)	Cs2 – O3	3.327(8)	Cs3 – O4^{xii}	3.400(4)
Cs1 – O6	3.410(4)	Cs2 – O3^{i}	3.327(8)	Cs3 – O4^{xiii}	3.339(4)
Cs1 – O6^{ii}	3.331(4)	Cs2 – O9^{ii}	2.952(4)	Cs3 – O8^{iv}	3.062(5)
Cs1 – O7^{iii}	3.148(4)	Cs2 – O9^{vi}	2.952(4)	Cs3 – O8^{xi}	3.062(5)
Cs1 – O8	3.342(5)				
Cs1 – O9^{ii}	3.278(4)				
Cs1 – O9^{iii}	3.173(4)				

Carbonate Group

C1 – O4	1.246(9)	∠ O4 – C1 – O6	117.5(5)
C1 – O6	1.294(6)	∠ O6 – C1 – O7	126.1(4)
C1 – O7	1.290(6)	∠ O7 – C1 – O4	116.4(5)

H_2O_2 -Molecules

O1 – O1^{v}	1.390(7)	O3 – O3^{v}	1.265(9)
O2^{i} – O5^{i}	1.413(7)	O8^{v} – O9^{v}	1.523(8)

Hydrogen Bonds

O1 – H1 ··· O4	2.761	∠ 162.0
O2 – H2 ··· O7	2.629	∠ 170.3
O3 – H3 ··· O4	2.749	∠ 156.4
O5 – H5 ··· O7	2.614	∠ 167.7
O8 – H8 ··· O6	2.669	∠ 164.2
O9 – H9 ··· O6	2.473	∠ 171.5

Symmetry codes: i) 1+x, y, z; ii) 0,5+x, -y, 0,5-z; iii) -0,5+x, -y, 0,5-z; iv) –x, -y, 1-z; v) 0,5-x, 0,5-y, z; vi) 1-x, 0,5+y, 0,5-z, vii) 1,5-x, 0,5-y, z; viii) -0,5-x, y, 0,5+z; ix) -1+x, 0,5-y, 0,5+z; x) -0,5-x, 0,5-y, z; xi) -0,5+x, 0,5+y, 1-z; xii) x, 0,5-y, 0,5+z; xiii) o,5-x, y, 0,5+z;

Tab. 3 Final atomic coordinates and U_{eq} for $Cs_2CO_3 \cdot 3\ H_2O_2$

	Wyckoff position	*x*	*y*	*z*	U_{eq}
Cs1	8e	0.2449(1)	0.0688(1)	0.3722(1)	0.0212(2)
Cs2	4d	3/4	1/4	0.3730(1)	0.0216(2)
Cs3	4d	-1/4	1/4	0.6221(1)	0.0220(2)
O1	8e	0.3255(8)	0.2187(3)	0.4862(3)	0.0333(10)
O2	8e	-0.1613(9)	0.1229(2)	0.4948(3)	0.0335(11)
O3	8e	0.1899(16)	0.2192(3)	0.2618(3)	0.0810(20)
O4	8e	0.2558(7)	0.1568(3)	0.1248(2)	0.0238(10)
O5	8e	-0.3389(8)	0.0675(3)	0.4949(3)	0.0351(11)
O6	8e	0.1565(7)	0.0505(2)	0.1842(2)	0.0246(9)
O7	8e	0.2636(6)	0.0470(2)	0.0751(2)	0.0221(9)
O8	8e	0.2522(7)	-0.1023(3)	0.2789(3)	0.0340(11)
O9	8e	0.2545(7)	-0.0907(2)	0.1943(3)	0.0284(10)
C1	8e	0.2571(9)	0.0833(4)	0.1280(2)	0.0162(17)

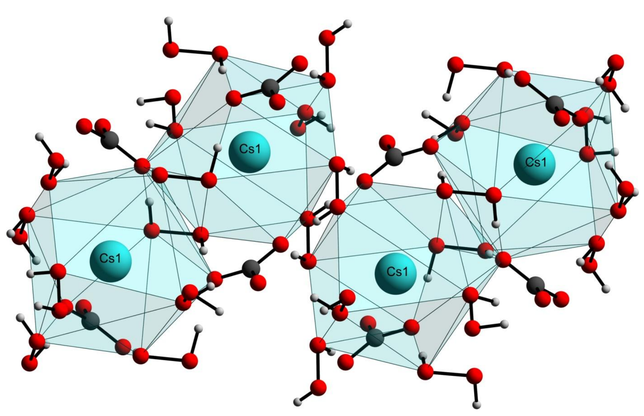

Fig. 2 Coordination polyhedra of Cesium 1

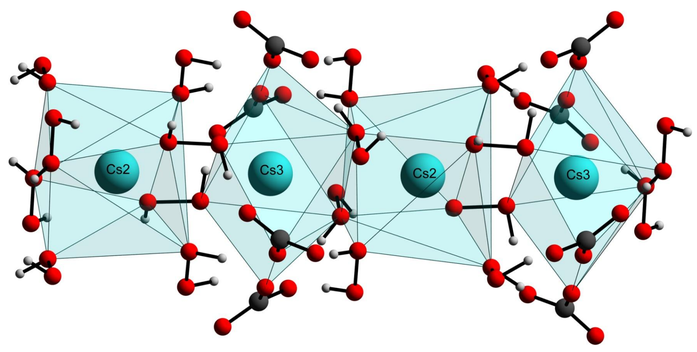

Fig. 3 Coordination polyhedra of Cesium 2 and 3

Vibrational characterization

A suitable single crystal was characterized by Raman Spectroscopy at low temperatures. The obtained spectrum and the assigned modes are shown below (Fig. 4 and Tab. 4).

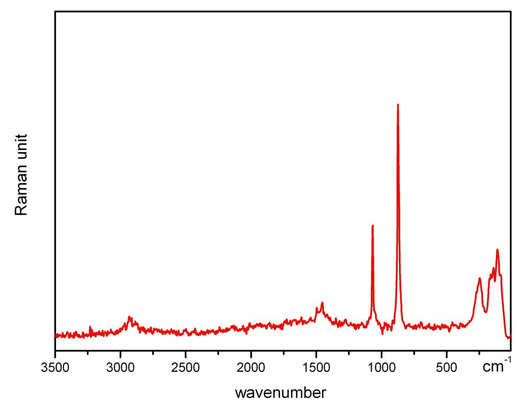

Fig. 4 Raman spectrum of $Cs_2CO_3 \cdot 3\ H_2O_2$

Tab. 4 Raman spectrum

modes	assignment
1453 w	ν_{as}(O-C-O)
1068 m	δ(O-C-O)
874 vs	ν (O-O) of H_2O_2
248 - 112 w	lattice vibrations

References

[1] J. M. Adams, R. G. Pritchard, Acta Crystallogr. Sect. B., **1979**, 33, 3650.

[2] V. Gwildies, diploma thesis, Clausthal University of Technology, **2007**.

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