TU Clausthal

Synthesis, Crystal Structure and Vibrational Characterization of Caesium Bis-μ-peroxo-tricarbonato-cerate(IV) Pentahydrate, $Cs_4[Ce(O_2)(CO_3)_3] \cdot 5\ H_2O$

Introduction

Dark red crystals of the title compound were obtained from saturated caesium carbonate solutions, hydrogen peroxide and Ce(IV) salts. These species were first described by Meloche [1, 2] in 1915. In 1985 and 1987 BARNES *et al.* [3, 4] synthesized the sodium- and potassium compounds and characterized their structures. They exhibit a general formula $A_4[Ce(O_2)(CO_3)_3] \cdot x\ H_2O$ (A = Na, K, Rb, Cs and x = 9, 6 ,6, 5). However, the structures of the heavier alkali metals have been unknown until the present work.

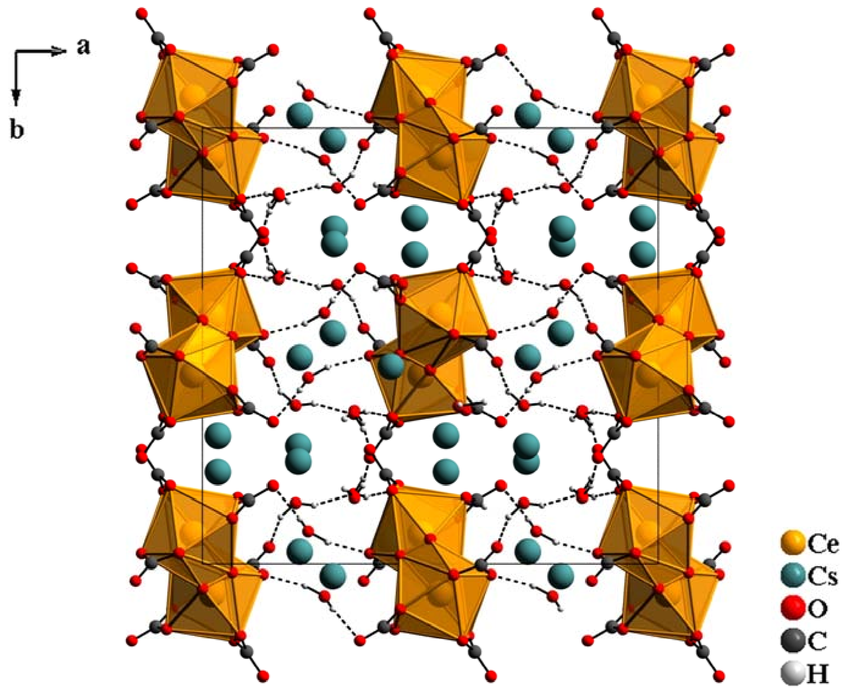

Fig. 1. Crystal structure of $Cs_4[Ce(O_2)(CO_3)_3] \cdot 5\ H_2O$ along [001] (dotted lines represent hydrogen bonds).

Experimental

$Cs_4[Ce(O_2)(CO_3)_3] \cdot 5\ H_2O$ was synthesized according to Meloche with slight modifications [1, 2]. Therefore 3 ml of 30% hydrogen peroxide were combined with 50 ml of a saturated caesium carbonate solution. $CeCl_3 \cdot 7\ H_2O$ (8.84 g, 23.7 mmol) were dissolved in 10 ml bidistilled water and then added dropwise under continuous stirring. Upon rapid heating a colour change from orange into dark red was observed at a point of 60°C. The mixture was heated as long as the colour deepened and a stream of carbon dioxide was passed through. After cooling to 0°C a rapid filtration followed. The resulting mixture was kept at room temperature and within two weeks dark red plate crystals appeared.

Structure description

The crystal structure of the caesium bis-μ-peroxo-tricarbonato-cerate(IV) pentahydrate crystallized in the orthorhombic space group *P*bca (No. 61) with eight formula units per unit cell and cell parameters: *a* = 19.384(2) Å, *b* = 18.528(2) Å, *c* = 10.487(3) Å and V_{EZ}= 3766.4(4) Å^3. The crystal structure consists of four symmetry-independent caesium ions, one unit of $[Ce(O_2)(CO_3)_3]^{4-}$ and five water molecules, which are involved in a hydrogen bonding network (Fig. 1).

Tab. 1. Crystallographic data for $Cs_4[Ce(O_2)(CO_3)_3] \cdot 5\ H_2O$

Crystal system	orthorhombic
Space group	*P*bca (No. 61)
Z	8
Lattice constants (*a* / Å)	19.384(2)
(*b* / Å)	18.528(2)
(*c* / Å)	10.487(3)
(*V* / Å^3)	3766.4(1)
Calculated density (g · cm^{-3})	3.435
Crystal size (mm^3)	0.25 x 0.30 x 0.14
Absorption correction method	empirical
Measuring diffractometer	STOE IPDS 2
Radiation / Mo-K_α / Å	0.71079
Reflections / parameters	3455 / 251
GooF	1.129
$R_1(I > 2\sigma(I))$, $wR_2(I > 2\sigma(I))$	0.0458, 0.0808
R1(all data), wR2(all data)	0.0674, 0.0862
Structure solution and	Programs SHELXS-97
Refinement	and SHELXL-97
e Å^3	1.551 / -1.595

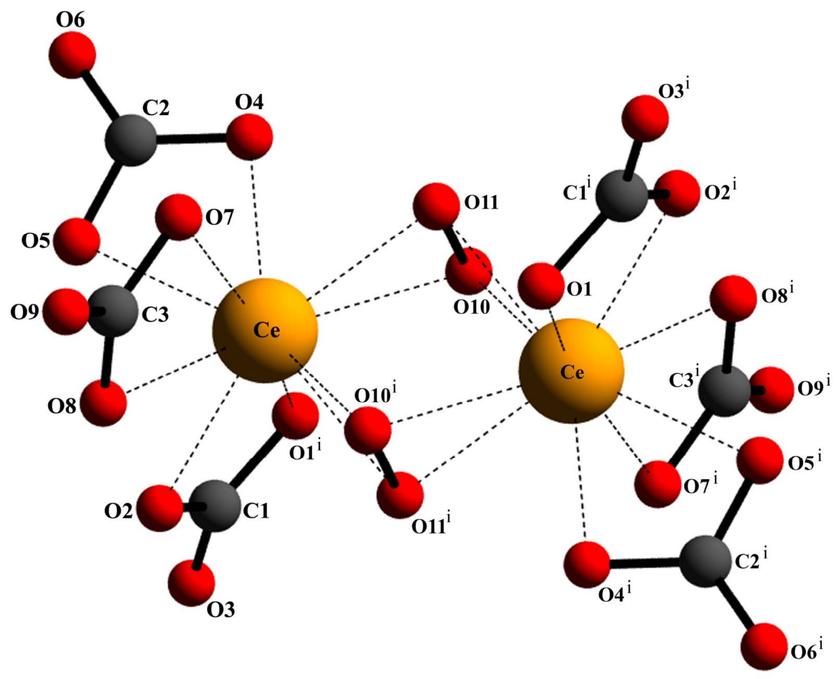

Fig. 2. The coordination of cerium in $Cs_4[Ce(O_2)(CO_3)_3] \cdot 5\ H_2O$ (dotted lines represent coordination bonds between cerium and oxygen).

Tab. 2. Bond length [Å] and angles [°] for $Cs_4[Ce(O_2)(CO_3)_3] \cdot 5\ H_2O$

Coordination of Cerium			
Ce - O10	2.348(1)	Ce - O8	2.418(1)
Ce - O11^{i}	2.355(1)	Ce - O4	2.418(1)
Ce - O10^{i}	2.359(1)	Ce - O2	2.421(1)
Ce - O11	2.387(1)	Ce - O5	2.462(1)
Ce - O7	2.417(1)	Ce - O1	2.467(1)
Carbonate-Group			
C3 - O9	1.234(1)	O1^{i} – C1 - O2	114.9(1)
C1 - O3	1.245(1)	O2 - C1 - O3	121.9(1)
C2 - O6	1.257(1)	O1^{i} – C1 - O3	123.1(1)
C2 - O4	1.292(1)	O4 - C2 - O5	114.4(1)
C3 - O8	1.297(1)	O5 – C2 - O6	122.0(1)
C1 - O2	1.299(1)	O4 – C2 - O6	123.6(1)
C2 - O5	1.308(1)	O7 - C3 - O8	114.6(1)
C3 - O7	1.309(1)	O7 – C3 - O9	122.1(1)
C1 - O1^{i}	1.309(3)	O8 - C3 - O9	123.3(1)
Peroxid-Group			
O10 - O11 1.472(1)			

Symmetry transformations: i) -x, -y, 1-z; ii) -x, -y, 2-z; iii) ½+x, y, 1½-z; iv) ½-x, -y, -½+z; v) ½+x, ½-y, 1-z; vi) ½-x, ½+y, z; vii) -x, ½+y, z; viii) x, ½-y, ½+z; ix) x, ½-y, ½+z;; x) -x, ½+y, 1½-z; xi) -½-x, ½+y, z; xii) ½-x, -y, ½+z; xiii) -½+x, y, 1½-z; xiv) x, y, 1+z; xv) -1½-x, -½+y, z; xvi) -x, -½+y, 1½-z

The coordination centre cerium is surrounded by ten oxygens of three bidentate carbonate groups and two doubly bidenate peroxide ions forming a slightly distorted bicappted tetragonal prism with a coordination number CN = 10 (8+2) (Fig.2). Two $[Ce(O_2)(CO_3)_3]^{4-}$ -polyhedrons are connected face-sharing through the oxygen atoms of the peroxide ions. Ce – O distances range from 2.348 to 2.467 Å . Carbonate groups exhibit C – O distances of 1.234 up to 1.309 Å and O – C – O angles between 114.4 and 123.7 ° (Table 2). The four symmetry-independent caesium ions are alternating coordinated by eight till nine oxygen atoms of carbonate groups, peroxide ions and water molecules with Cs – O distances from 3.01 to 3.5587 Å (Fig. 4).

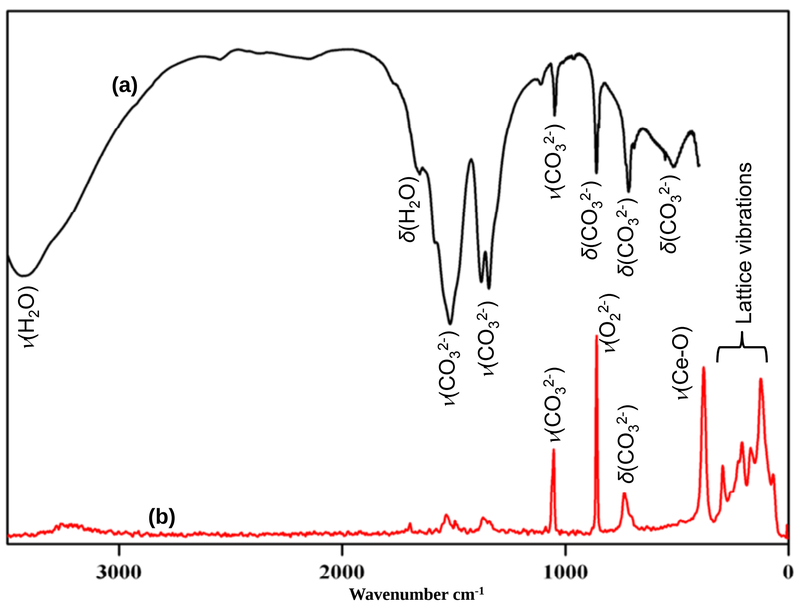

Fig. 3. FT-IR (a) and RT-Raman (b) of $Cs_4[Ce(O_2)(CO_3)_3] \cdot 5\ H_2O$.

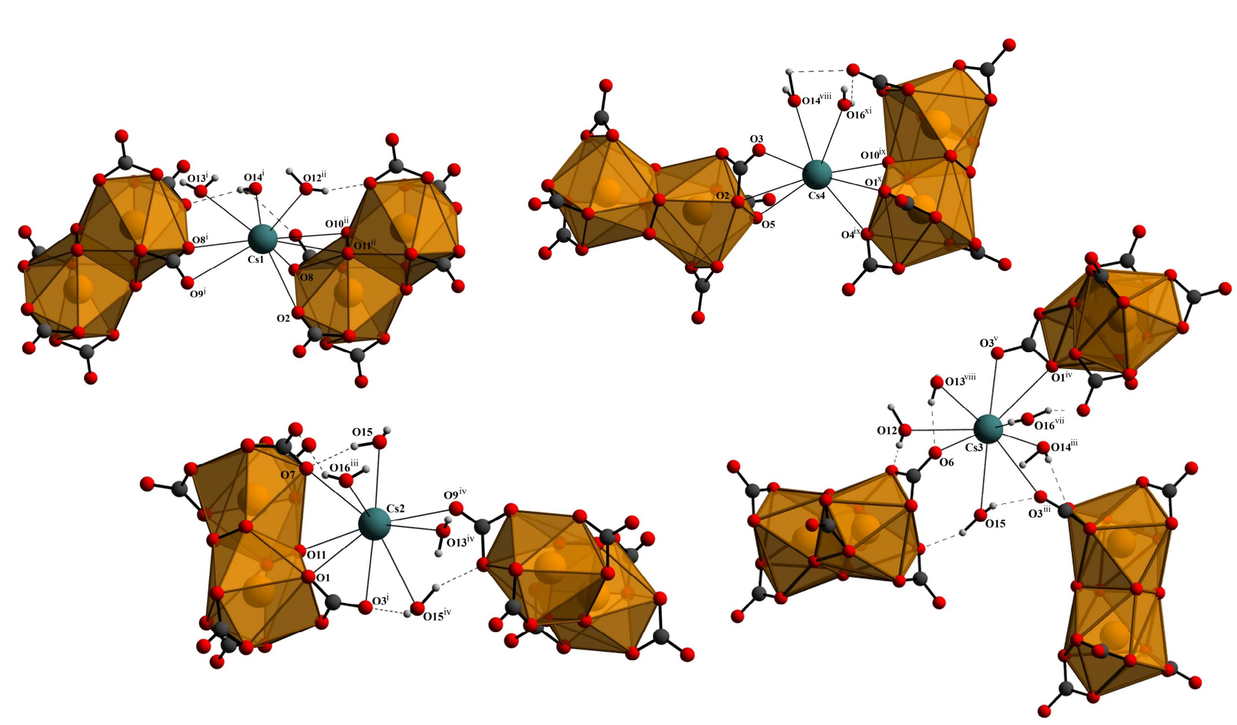

Fig. 4. Coordination sphere of caesium atoms in $Cs_4[Ce(O_2)(CO_3)_3] \cdot 5\ H_2O$ (dotted lines represent hydrogen bonds).

References

[1] C. C. Meloche, J. Am. Chem. Soc., **37** (1915) 2338

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[3] J. C. Barnes, C. S. Blyth, Inorg. Chim. Acta, **110** (1985) 133

[4] J. C. Barnes, C. S. Blyth, D. Knowles, Inorg. Chim. Acta, **126** (1987) L3-L6

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