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Cesium Hydroperoxostannate: First Complete Structural Characterization of a Homoleptic Hydroperoxocomplex

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The crystal structure of cesium hexahydroperoxostannate $Cs_2Sn(OOH)_6$ is presented. The compound was characterized by single crystal and by powder X-ray diffraction, FTIR, ^{119}Sn MAS NMR, and TG-DTA. $Cs_2Sn(OOH)_6$ crystallizes in the trigonal space group $P\bar{3}$, $a = 7.5575(4)$, $c = 5.1050(6)$ Å, $V = 252.51(4)$ Å^3, $Z = 1$, $R_1 = 0.0120$ ($I > 2\sigma(I)$), $wR_2 = 0.0293$ (all data), and comprises cesium cations and slightly distorted octahedral $[Sn(OOH)_6]^{2-}$ anions lying on the threefold axis. The $[Sn(OOH)_6]^{2-}$ unit forms 12 inter-anion hydrogen bonds resulting in anionic chains spread along the *c*-axis. All six hydroperoxo ligands are crystallographically equivalent; O−O distances are 1.482(2), only slightly longer than the O−O distance in hydrogen peroxide. FTIR and ^{119}Sn MAS NMR reveal the similarity between all alkali hydroperoxostannates.

Hydrogen peroxide is a friendly oxidation agent which also plays a significant role in life science. However, it is a stable nucleophile and its activation usually goes through coordination to a metal center, similar to its biocatalytic activation by a heme center.[1] Many transition metal−dioxygen complexes have been reported, but the crystalline structures of only a few of them were determined. Most of this data pertains to peroxo complexes, and only 14[2] hydroperoxo−transition metal complexes were reported. Nontransition element−dioxygen complexes are much less researched, despite their importance as reagents and catalysts. Borate catalyzes sulfide oxidations by hydrogen peroxide through hydroperoxo and peroxoborate intermediates.[3] It was suggested that aluminum catalysis of the epoxidation process with hydrogen peroxide goes through the Al-OOH site, an intermediate responsible for the activation of the hydrogen peroxide and oxygen transfer.[4] Sn(IV) catalyzes the Baeyer−Villiger oxidation with hydrogen peroxide.[5] Despite that, to date only about 20 of the peroxo-bridged nontransition element crystalline structures have been reported in addition to peroxodicarbonates, peroxodisulphates, and peroxodiphosphates. Peroxocompounds of boron,[6] silicon,[7] gallium,[8] germanium,[9] tin,[10] antimony[11] tellurium,[12] and bismuth[13] were characterized by X-ray diffraction. Only one crystalline structure of the nontransition element hydroperoxo compound $Rb_2Sn(OOH)_6$ was reported.[14] The H-atoms were not localized in this crystalline structure, and thus the hydrogen bonding which is responsible for structure formation remained unclear. In recent articles[15,16] we have described ^{119}Sn NMR studies that showed that hexahydroperoxostannate anion, $[Sn(OOH)_6]^{2-}$, is formed by gradual substitution of the

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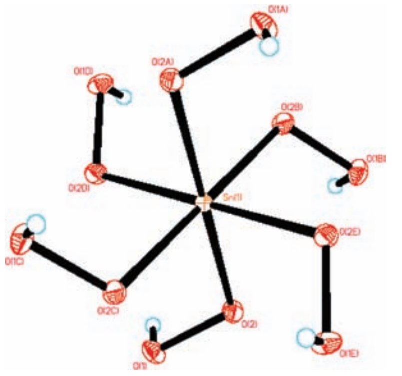

Figure 1. Structure of $[Sn(OOH)_6]^{2-}$. Displacement ellipsoids are drawn at 50% probability level.

hydroxo ligands of hydroxostannate precursor by reaction with hydrogen peroxide. Sodium, potassium, and rubidium hydroperoxostannates were obtained by this route and characterized by Raman, IR, EXAFS, Mossbauer, and ^{119}Sn NMR spectroscopies.[17−19] As far as we know, hexahydroperoxostannates are the only examples of homoligand hydroperoxo complexes known today.

Cesium hydroperoxostannate $Cs_2Sn(OOH)_6$ (**1**) was obtained by reaction of cesium hydroxostannate with concentrated hydrogen peroxide.[20] Cesium hydroxostannate was synthesized from $SnCl_4$ by a procedure that was described for potassium hydroxostannate.[21] The structure[22] of **1** consists of cesium cations and $[Sn(OOH)_6]^{2-}$ anions lying on a 3-fold axis. The $[Sn(OOH)_6]^{2-}$ octahedron is slightly distorted with *cis*-O−Sn−O angles varying within 87.77(6)−92.23(6)° (Figure 1). In the anion, all six hydroperoxo ligands are crystallographically equivalent. The Sn−O distance (2.075(1) Å) is somewhat longer than that in alkali metal hexahydroxo stannates $M_2Sn(OH)_6$ (2.060(1) Å[21] and 2.068(1) Å[23] for K, 2.074(4) Å[21] for Na, 2.039(2)−2.055(2) Å[24] and 2.053(1)−2.075(1) Å[25] for Li). The peroxide O(1)−O(2) bond length is 1.482(2). This value is ∼0.02 Å greater than those previously observed in the accurately determined structures of crystalline H_2O_2 (1.461(3) Å),[26] urea perhydrate (1.4573(8) Å),[27] and serine perhydrate (1.461(2) Å).[28] However, the O−O distance in anion **1** is noticeably shorter than the O−O bond lengths (1.50(1)−1.54(1) Å) in uncharged μ_2-peroxo complexes of tin $\{[(SiMe_3)_2X]_2Sn\}(\mu_2\text{-}O_2)_y(\mu_2\text{-}O)_{2-y}$ ($X = CH, N$; $y = 1, 2$).[10] The Sn−O(2)−O(1)−H fragment adopts a skewed conformation with the value of the torsion angle equal to 96(2)°. No intra-anion hydrogen bonds were observed in **1**.

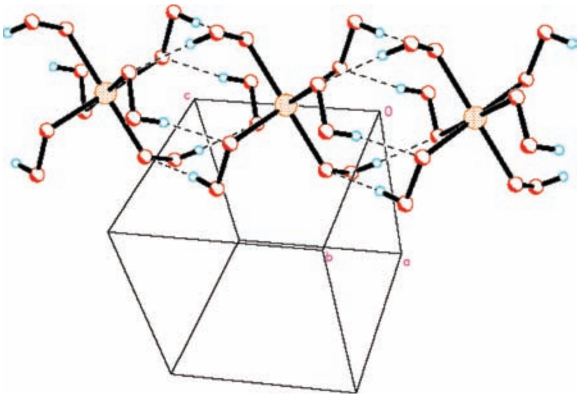

Figure 2. Hydrogen-bonded anionic chains in the structure of **1**.

In the crystal, $[Sn(OOH)_6]^{2-}$ anion forms three acceptor (O(2)···H−O(1)) and three donor (O(1)−H···O(2)) hydrogen bonds with both neighboring (along *c*-axis) hexahydroperoxostannate anions (Figure 2). This type of interanion interaction motif may be called "sixfold hydroperoxo embraces" (in analogy to "sixfold phenyl embraces" for intercation $Ph_4P^+\cdots Ph_4P^+$ interactions[29]). The separation between the closest anion centers is equal to the *c* unit cell dimension (5.1050(6) Å). Thus, all hydrogen atoms are involved in hydrogen bonding, and every $Sn(OOH)_6{}^{2-}$ anion forms 12 strong intermolecular hydrogen bonds resulting in formation of anionic chains spread along the threefold axis.

Cesium cations occupy the space between anionic chains (Figure 3). Cs atoms are η^2-bonded to three hydroperoxo ligands (3.052(2) and 3.214(2) Å). Furthermore, Cs cations are linked with nine OOH units in η^1-mode (3.169(2),

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(20) Cesium hexahydroperoxo stannate, $Cs_2Sn(OOH)_6$, was synthesized by dissolution of 1.0 g of cesium hydroxostannate in 2 mL (70 wt %) of hydrogen peroxide and crystallization in a desiccator over P_2O_5 for one week. The obtained powder was separated from the mother liquor on a glass filter and washed three times with ethanol and one time with diethyl ether and dried in vacuum desiccator (1.05 g, 88%). The product was confirmed by chemical analysis (active oxygen, potassium, and tin content) and X-ray powder diffraction. Average active oxygen content was estimated by permanganatometry. Cesium and tin abundances were determined by gravimetric analysis as cesium tetraphenylborate and SnO_2, respectively. Anal. Calcd for $H_6O_{12}SnCs_2$: O_{act}, 16.48; Cs, 45.63; Sn, 20.38. Found: O_{act}, 15.53; Cs, 44,70; Sn, 21.02. XRD patterns of **1** powder fit well the X-ray diffractogram calculated from single crystal data of **1**. The only exceptions are three small additional peaks ($d = 4.860$, 2.979, and 2.436 Å) corresponding to cesium chloride impurity. Cesium peroxystannate powder is stable at room temperature (no weight loss during a month in a closed beaker), reveals a small weight loss under heating, and decomposes by an autocatalytic exothermic reaction at 98 °C according to TG and DSC data. A crystal of **1** suitable for X-ray analysis was obtained from the solution prepared by dissolution of cesium hydroperoxo stannate powder in concentrated (98%) H_2O_2.

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(22) Crystal data for **1**: $Cs_2H_6O_{12}Sn$, $M = 582.56$, trigonal, $a = 7.5575(4)$, $c = 5.1050(6)$ Å, $V = 252.51(4)$ Å^3, space group $P\bar{3}$, $Z = 1$, $D_c = 3.831$ g/cm^3, $F(000) = 262$, $\mu(\text{Mo K}\alpha) = 9.688$ mm^{-1}, colorless needle with dimensions approximately 0.35 × 0.02 × 0.02 mm. A total of 2302 reflections (452 unique, $R_{int} = 0.0166$) were measured on a Bruker SMART APEX II diffractometer (graphite monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å) at 150 K using ω scan mode. The structure was solved by direct methods and refined by full matrix least-squares on F^2 (SHELXTL) with anisotropic thermal parameters for all non-hydrogen atoms. Atom H(1) was found from difference Fourier synthesis and refined isotropically. The final residuals were $R_1 = 0.0120$ for 434 reflections with $I > 2\sigma(I)$; $wR_2 = 0.0293$ for all data and 28 parameters. GOF = 1.141, max/min $\Delta\rho = 0.376/-0.757$ e × Å^{-3}.

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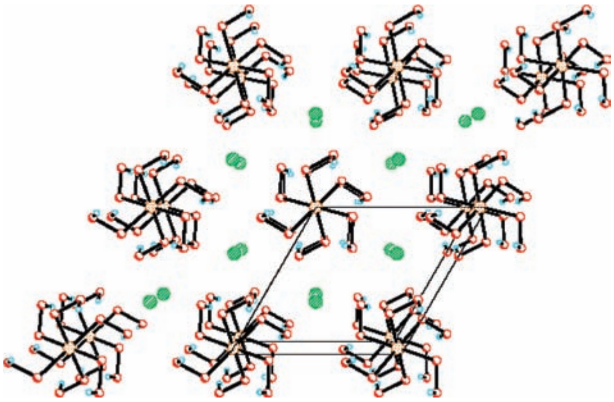

Figure 3. Arrangement of Cs cations (green circles) between anion chains (view along *c*-axis) in the structure of **1**.

3.427(2), and 3.671(2) Å) resulting in a total coordination number of 15.

Despite the resemblance of the unit cell dimensions of **1** with those of the poorly determined structure of $Rb_2Sn(OOH)_6$[14] (**2**), these compounds are not isomorphous. However, the packing motif in **2** is similar to that found for **1**: hexahydroperoxostannate anions form anionic chains with Sn···Sn separation equal to 5.033(2) Å.

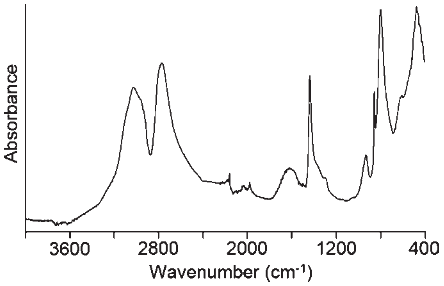

Figure 4. FTIR spectrum of **1**.

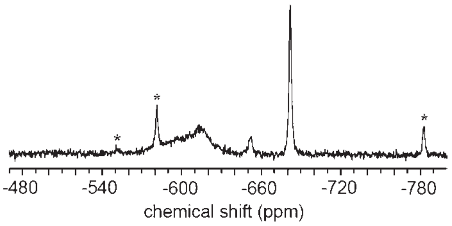

Figure 5. ^{119}Sn MAS NMR spectrum of **1**. Asterisks denote spinning side bands.

The FTIR spectrum of **1** (Figure 4) is similar to those for sodium, potassium, and rubidium hydroperoxo stannates[15,19] and exhibits two broad and intensive bands in the wavenumber range 4000–1800 cm^{-1} with absorbance maxima at 3030 and 2780 cm^{-1}. The 3030 cm^{-1} band with shoulders at 3100 and 2960 cm^{-1} is attributed to O–H stretching of the OOH group in **1**. The band with maximum at 2780 cm^{-1} is typical for hydrogen peroxide and its species and corresponds to the combination mode $\nu_2 + \nu_6$ of hydroperoxo groups.[30] A broad weak band with absorbance at about 1630 cm^{-1} might be assigned to δ(H–O–H) vibrations of water produced by decomposition of the hydroperoxostannate sample. An intensive maximum at 1440 cm^{-1} is attributed to the δ(O–O–H) of hydroperoxo groups in **1**. The small absorbance maximum at 934 cm^{-1} probably represents a partial decomposition of the sample and can be assigned to the δ (Sn–O–H) vibrations, although there is no noticeable absorbance at 3400 cm^{-1}. A weak sharp band at 856 cm^{-1} corresponding to O–O stretching appears in the FTIR spectrum due to the slight distortion of the $[SnO_6]$ octahedron. This peak maximum is shifted compared to solvated and free hydrogen peroxide (880 cm^{-1}).[30] An intensive band at 800 cm^{-1} can be attributed to the δ(Sn–O–O) vibrations of anion $[Sn(OOH)_6]^{2-}$. The absorbance in this FTIR area is typical for other alkali metal hydroperoxostannates.[15,19] The bands at 450–700 cm^{-1} correspond to the different modes of the Sn–O stretching.

The ^{119}Sn MAS NMR study of **1** (Figure 5) corroborates the previously obtained ^{119}Sn NMR results for solid and liquid systems of rubidium and potassium peroxostannates.[15,16] The ^{119}Sn MAS NMR spectrum of crystalline $Cs_2Sn(OOH)_6$ is very similar to that for $K_2Sn(OOH)_6$[15] and shows the most intensive signal with chemical shift −681 ppm corresponding to the $[Sn(OOH)_6]^{2-}$ in **1**. The small signal at $\delta = -651$ ppm and broad signal with maximum at $\delta = -615$ ppm are attributed to the decomposition products formed by the high rate spinning during the MAS NMR measurements.

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Supporting Information Available: CIF file containing X-ray crystallographic data, selected crystallographic data, TG DTA, and X-ray powder diffraction data for **1**, and experimental details.This material is available free of charge via the Internet at http://pubs.acs.org.

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