

Sodium tetrahydroxoplumbate $\text{Na}_2[\text{Pb}(\text{OH})_6]$: synthesis, structure, and properties

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Abstract

By the interaction of lead dioxide, sodium hydroxide and water, sodium tetrahydroxoplumbate(IV) of the composition $\text{Na}_2[\text{Pb}(\text{OH})_6]$ was isolated in the form of single crystals sized up to 2.0 mm. The compound was identified by a set of methods: chemical analysis, optical analysis, X-ray powder analysis, X-ray single crystal analysis, IR spectroscopy, thermogravimetric analysis. The picnometric density was measured as 3.92 g/cm³. $\text{Na}_2[\text{Pb}(\text{OH})_6]$ crystallizes as transparent colorless anisotropic single axis and optically positive crystals. Mean transmittance coefficient 1.684±0.005. The X-ray gramme was indexed as a hexagonal symmetry with the cell parameters: $a = 6.020 \pm 0.09 \text{ \AA}$; $c = 14.22 \pm 0.02 \text{ \AA}$; $V = 446 \text{ \AA}^3$. The corresponding parameters found by the X-ray single crystal analysis were detected as following: $a = 6.0361 \pm 0.0005 \text{ \AA}$, $c = 14.253 \pm 0.002 \text{ \AA}$, $V = 449.72 \pm 0.09 \text{ \AA}^3$ with three molecules in a unit cell; space group $R\bar{3}$. The base of the crystal structure are almost regular lead-oxygen octahedra and sodium cations which are posed in the way that oxygen atoms also form an octahedron around each Na^+ species. Sodium-oxygen octahedra are distorted. Two crystallographically nonequivalent sodium atoms are localized in the octahedra with the different interatomic Na–O distances: 2.419(11) Å and 2.423(11) Å, respectively. Lead-oxygen octahedra are characterized by the six same Pb–O distances (2.165(10) Å, and valence angles O–Pb–O* 93.3(4)° and O*–Pb–O** 86.7(4)°. The lead- and sodium-oxygen octahedra form unlimited layers along the Z-axis. The O–H bond length in the hydroxyl-group equals 0.85 Å. The O–H bond vector is perpendicular to the plane of the lead-sodium-oxygen layer. Thus, the layers interact with each other through the hydrogen bonds in the way that each OH group acts both as hydrogen donor and hydrogen acceptor. The thermolysis of $\text{Na}_2[\text{Pb}(\text{OH})_6]$ proceeds in the temperature interval from 140 to 570 °C in two stages according to the scheme: $2\text{Na}_2[\text{Pb}(\text{OH})_6] \rightarrow \text{Na}_2\text{Pb}_2\text{O}_5 + 2\text{NaOH} \rightarrow 2\text{Na}_2\text{PbO}_3$. As a result, the $\beta\text{-Na}_2\text{PbO}_3$ modification is formed. The mentioned compound is also thermally unstable, and decomposes at 890 °C with the release of oxygen.

References

- [1] V.K. Ivanov. The functional nanomaterials on the basis of dioxides of cerium and elements of subgroup of a titanium: Synthesis, research of structure and size effects. Abstract of the PhD Thesis in chemical sciences: 02.00.01. Ivanov Vladimir Konstantinovich. Moscow. 2011. 48p.
- [2] Din Zung Tkhe, S.A. Bahteev, and R.A. Yusupov. Changing the pH of the solution in the system $\text{Pb}(\text{II})\text{-H}_2\text{O}\text{-OH}$ –by hydrolysis of precipitation $\text{Pb}_5(\text{OH})_x\text{H}_2\text{O}_y(\text{An})_z$. *Butlerov Communications*. 2014. Vol.38. No.6. P.164-168. ROI: jbc-02/14-38-6-164
- [3] S.A. Onorin, D.A. Kazakov, and A.V. Portnova. Research of zirconium tetrabutoxide hydrolysis in aqueous-alcoholic medium. *Butlerov Communications*. 2012. Vol.32. No.12. P.35-38. ROI: jbc-02/12-32-12-35

- [4] V.D. Maximov, A.S. Shaporev, V.K. Ivanov, B.R. Churagulov, Yu.D. Tretyakov. Hydrothermal synthesis of nanocrystal anatase from aqueous solutions of titanyl sulfate for photocatalytic applications. *Chemical technology*. **2009**. No.2. P.70-75. (russian)
- [5] Yahya Absalan, O.V. Avramenko, and O.V. Kovalchukova. Optimization of the ways of synthesis of the catalysts based on titanium dioxide by the thermal decomposition of titanium tetrabutoxide. *Butlerov Communications*. **2016**. Vol.47. No.8. P.49-55. ROI: jbc-02/16-47-8-49
- [6] B.N. Ivanov-Emin, A.M. Ilyinets, B.E. Zaytsev, A.V. Kostrikin, F.M. Spiridonov, V.P. Dolganev. Hexahydroxoplumbats (IV) alkali metals. *Zhurn. Anorg. Chemistry*. **1990**. Vol.35. No.9. P.2285. (russian)
- [7] H. Zocher. Über zinnsaure und bleisaure Salze.... der Chemie der Zinn-und Bleisaurecher. *Z. Anorg. Allg. Chem.* **1920**. B.112. P.1.
- [8] B.N. Ivanov-Emin, A.V. Kostrikin, F.M. Spiridonov, I.V. Linko, A.I. Ezhov, R.V. Kuznetsova. Hexahydroxogafnat of a potassium. *Zhurn. Anorg. Chemistry*. **1996**. Vol.41. No.11. P.1812. (russian)
- [9] H. Jacobs, R. Stahl. Neubestimmung der Kristallstrukturen der Hexahydroxometallate $\text{Na}_2\text{Sn}(\text{OH})_6$, $\text{K}_2\text{Sn}(\text{OH})_6$ und $\text{K}_2\text{Pb}(\text{OH})_6$. *Z. Anorg. Allg. Chem.* **2000**. B.626. P.1863.
- [10] E. Freymy. *Ann. Chim. Phys.* **1844**. Vol.3. No.12. P.457 is quoted on [7].
- [11] O. Seidel. *J. Prakt. Chem.* **1879**. B.20. Vol.2. P.200 is quoted on [7].
- [12] Gmelins Handbuch der anorg. Chem. *Springer-verlag*. **1974**. No.47. 1212p.
- [13] G. Grube. Über das chemische und electrochemische verhalten der bleisauren salze. *Z. Elektrochem.* **1922**. B.28. P.273.
- [14] A. Simon. Über die Kostitution von Natriumplumbat. *Z. Anorg. Allg. Chem.* **1929**. B.177. P.109.
- [15] Guide to inorganic synthesis. Under the editorship of the Brouwer G. M.: *World*. **1986**. Vol.6. 2222p.
- [16] G. Sharlo. Methods of analytical chemistry. *M.: Chemistry*. **1969**. Ch.1,2. 1204p. (russian)
- [17] F.V. Syromyatnikov. Micropicometric method of definition of a specific gravity of minerals. *Min. Raw materials*. **1930**. No.6. P.905. (russian)
- [18] S.I. Troianov, A.V. Kostrikin, I.V. Linko, B.E. Zaytsev, A.I. Ezhov, F.M. Spiridonov. Crystal structure of Hydroxogafnat of $\text{Na}_2\text{Hf}(\text{OH})_6$ and $\text{K}_2\text{Hf}(\text{OH})_6$. *Crystallography*. **1999**. Vol.44. No.6. P.1054. (russian)
- [19] M. Trömel, E. Lupprich. Die Kristallstruktur von $\text{Li}_2\text{Pt}(\text{OH})_6$ und $\text{Na}_2\text{Pt}(\text{OH})_6$. *Z. Anorg. Allgem. Chem.* **1975**. B.414. P.160.
- [20] G. Lang. Die Kristallstruktur einiger Vertrefen der Verbindungsklasse $\text{M}_2\text{M}^{\text{IV}}\text{O}_3$ als Beitrag zur Aufklärung der Ordnungsphase von Li_2TiO_3 . *Z. Anorg. Allg. Chem.* **1954**. B.276. P.77.