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Synthesis and Properties of Lead(II) 1-Hydroxyethane-1,1-diphosphonate(2–) Monohydrate

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Abstract — Conditions for isolation of a 1-hydroxyethane-1,1-diphosphonic acid (H_4L) complex of the composition $PbH_2L \cdot H_2O$ from aqueous solutions of various composition are studied. The X-ray analysis of the resulting polycrystalline sample showed that it is single-phase. The IR spectrum is presented, and the solubility and thermal transformations of the sample are studied.

Polarographic and potentiometric studies of complex formation of Pb^{2+} with 1-hydroxyethane-1,1-diphosphonic acid $CH_3C(OH)(PO_3H_2)_2$ (H_4L) in aqueous solutions revealed the formation of PbL^{2-}, Pb_2L, and some other complexes [1, 2]. Solid $Pb_2L \cdot 2H_2O$ [3] and $PbH_2L \cdot H_2O$ [4] were isolated. The latter compound was obtained by the reaction of lead carbonate with a 30% aqueous solution of H_4Li in a 1:1 molar ratio, followed by slow evaporation of the mixture at room temperature. The complex $PbH_2L \cdot H_2O$ forms monoclinic crystals of the space group $P2_1/c$ with the following unit cell parameters: a 10.896(6) Å, b 8.297(5) Å, c 10.317(6) Å, β 109.82(6)°, and $Z = 4$ [4]. The Pb^{2+} ion coordinates six phosphonate oxygen atoms of one bidentate and four monodentate ligands H_2L^{2-} (partial dentacity). Each of them is bound with five Pb^{2+} ions, exhibiting the total dentacy equal to four.[1] The molecules of crystallization water do not enter into the coordination sphere of Pb^{2+} but form hydrogen bonds with the hydroxyl oxygens and the phosphonate oxygens and hydrogens of the ligand [4].

In the present work we studied conditions of formation and some properties of the complex $PbH_2L \cdot H_2O$.

The pattern calculated from single-crystal X-ray diffraction data [4] coincides with the experimental powder X-ray diffraction pattern of $PbH_2L \cdot H_2O$ (see table). This fact together with the elemental analysis shows that the polycrystalline sample is single-phase.

The $PbH_2L \cdot H_2O$ sample consists of concretions and separate sphenic crystals up to 3 mm in length. The complex is soluble in ammonia and alkalis, ethylenediaminetetraacetate solutions, and hydrochloric, sulfuric (with decomposition), and nitric acids. It is poorly soluble in water, acetic acid, DMSO, DMF, glycerol, ethanol, isopropanol, ethyl acetate, acetone, dioxane, carbon tetrachloride, and benzene. The poor solubility of the complex in nondestructive polar solvents is consistent with its polymeric structure. The complex is nonhygroscopic and stable on handling in air.

From the aqueous solution with C^0_{Pb} = 0.3 M and a 1:1 molar ratio of $Pb(NO_3)_2$ and H_4L, fine crystals immediately precipitate and then gradually pass into heavy concretions of coarse lustrous crystals; by elemental analysis and X-ray powder diffraction, the latter are a single-phase complex $PbH_2L \cdot H_2O$. When the reagent molar ratio is increased to 1 : 3, the composition of the precipitate remains the same (yield 98%). Lead carbonate dissolves in a large excess (1 : 3) of aqueous H_4L.

$$PbCO_3 + 2H_4L \rightarrow Pb(H_3L)_2 + H_2O + CO_2\uparrow.$$

However, here, too, the precipitate also contains nothing more than $PbH_2L \cdot H_2O$.

$$Pb(H_3L)_2 + H_2O \longrightarrow PbH_2L \cdot H_2O\downarrow + H_4L.$$

Probably, the isolation of $Pb(H_3L)_2 \cdot nH_2O$ was precluded by the poor solubility of $PbH_2L \cdot H_2O$ in water and dilute HNO_3, and also the low thermodynamic stability of $Pb(H_3L)_2$ in solution. At the same time, stoichiometric $M(H_3L)_2 \cdot nH_2O$ complexes are known for many bivalent metals [6–9].

According to differential thermal analysis (see

[1] The definition of ligand dentacity was taken from [5].

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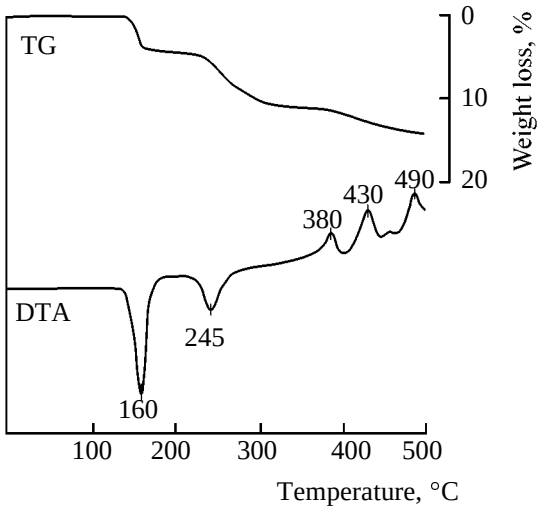
Powder X-ray diffraction results for $PbH_2L \cdot H_2O$[a]

d, Å		*I*, %		*h k l*	*d*, Å		*I*, %		*h k l*
experiment	calculation	experiment	calculation		experiment	calculation	experiment	calculation	
10.23	10.251	100	100	1 0 0		2.334		1	3 1 2
	5.125		2	2 0 0	2.332	2.334	2	4	1 2 3
5.11	5.107	5	5	$\bar{1}$ 0 2	2.298	2.305	0.5	1	$\bar{3}$ 1 4
4.848	4.853	6	19	0 0 2		2.300		1	2 1 3
4.484	4.491	3	5	$\bar{2}$ 1 1	2.276	2.276	2	3	2 3 1
4.353	4.360	2	2	2 1 0	2.209	2.210	2	2	4 1 1
4.324	4.333	2	6	$\bar{2}$ 0 2	2.200	2.200	1	1	$\bar{3}$ 3 1
4.179	4.189	0.6	1	0 1 2		2.200		1	1 0 4
3.904	3.904	7	20	1 0 2	2.124	2.126	0.5	2	1 1 4
	3.841		4	$\bar{2}$ 1 2	2.112	2.112	1	2	$\bar{4}$ 2 3
3.811	3.815	7	14	0 2 1		2.100		1	$\bar{5}$ 1 2
3.742	3.742	10	20	$\bar{1}$ 2 1		2.096		1	$\bar{4}$ 1 4
3.604	3.607	2	2	2 1 1	2.091	2.090	2	1	$\bar{5}$ 1 1
3.528	3.533	1	2	1 1 2	2.072	2.074	2	2	0 4 0
	3.429		4	1 2 1		2.073		1	2 2 3
3.419	3.417	4	2	3 0 0	2.032	2.033	1	2	1 4 0
3.382	3.386	5	9	$\bar{3}$ 0 2		2.017		1	$\bar{5}$ 1 3
3.325	3.327	3	4	$\bar{3}$ 1 1	2.011	2.010	2	2	3 3 1
3.274	3.276	15	24	$\bar{2}$ 2 1	1.990	1.990	2	2	5 1 0
3.160	3.159	3	3	$\bar{3}$ 1 0	1.949	1.952	1	1	2 0 4
3.135	3.135	2	3	$\bar{3}$ 1 2		1.947		1	4 1 2
3.046	3.046	3	5	2 0 2		1.923		2	$\bar{2}$ 4 0
2.879	2.882	1	2	2 2 1	1.992	1.992	2	2	$\bar{1}$ 4 2
2.858	2.859	2	4	2 1 2		1.921		1	$\bar{4}$ 3 2
2.759	2.760	2	2	$\bar{3}$ 1 1	1.907	1.907	0.5	2	0 4 2
2.730	2.733	3	3	$\bar{3}$ 2 1	1.870	1.871	1	2	$\bar{2}$ 4 2
	2.728		2	$\bar{3}$ 1 3		1.870		1	$\bar{5}$ 1 4
2.670	2.671	3	2	$\bar{4}$ 0 2	1.845	1.846	0.5	2	$\bar{2}$ 2 5
	2.670		2	1 3 0		1.835		1	5 1 1
2.644	2.647	4	11	$\bar{1}$ 2 3	1.831	1.832	1	1	$\bar{1}$ 4 2
	2.581		2	$\bar{4}$ 1 1		1.829		2	$\bar{1}$ 2 5
2.572	2.575	3	5	$\bar{2}$ 2 3		1.827		1	$\bar{3}$ 3 2
	2.564		2	$\bar{1}$ 0 4	1.805	1.805	0.3	1	$\bar{3}$ 2 5
	2.553		2	$\bar{2}$ 0 4	1.774	1.774	1	0.8	$\bar{6}$ 1 2
2.547	2.551	3	6	0 2 3		1.773		0.8	$\bar{3}$ 4 0
	2.542		2	$\bar{4}$ 1 2	1.769	1.769	1	0.9	$\bar{3}$ 4 2
2.449	2.456	5	3	$\bar{2}$ 3 1	1.757	1.758	0.5	2	0 2 5
	2.449		3	4 1 0	1.741	1.741	0.5	1	$\bar{6}$ 1 3
	2.434		2	2 3 0	1.716	1.719	0.5	1	$\bar{2}$ 0 6
2.432	2.432	2	1	3 0 2	1.704	1.702	1	1	$\bar{5}$ 3 1
	2.427		1	0 0 4	1.686	1.688	0.3	1	$\bar{1}$ 0 6
	2.399		3	$\bar{3}$ 0 4	1.659	1.659	1	1	$\bar{6}$ 1 4
2.392	2.392	3	4	$\bar{3}$ 2 1	1.649	1.651	0.3	1	$\bar{1}$ 2 5
2.368	2.371	1	3	$\bar{3}$ 2 3	1.610	1.613	0.5	1	$\bar{1}$ 4 4
2.352	2.354	0.5	1	$\bar{4}$ 1 3	1.576	1.577	0.5	1	0 4 4

[a] Interplanar distances (*d*) corresponding to reflections with $I > 1\%$ are presented. I_{exp} relate to peak heights on the X-ray powder pattern. I_{calc} relate to integral intensities of the reflections.



Thermoanalytical curves for $PbH_2L \cdot H_2O$.

figure) and isothermal gravimetry, dehydration of $PbH_2L \cdot H_2O$ begins only at 145°C (DTA_{min} 160°C). Holding the powder of $PbH_2L \cdot H_2O$ at 185°C to constant weigh results in a weight loss (found 4.4%, calculated 4.20%) corresponding to the formation of anhydrous lead(II) 1-hydroxyethane-1,1-diphosphonate(2–). The thermal decomposition of the complex with P–C bond cleavage in the ligand H_2L^{2-} begins at 220°C and is accompanied by an endothermic effect (DTA_{min} 245°C). The thermal stability of PbH_2L is only slightly lower than those of compounds containing the H_2L^{2-} anion and alkali metal cations [10–12].

EXPERIMENTAL

The IR spectrum was recorded on a UR-20 spectrometer for a suspension in Vaseline oil in the range 4000–400 cm^{-1}. The X-ray diffraction patterns were obtained on a DRON-3 diffractometer (CuK_α radiation, Ni filter, 2θ 3–60°. Thermal analysis was performed on a Q-1500 derivatograph (ceramic crucible, sample 250 mg) under nitrogen at a heating rate of 5 deg/min in the range 20–500°C. Elemental analysis was carried out on a CHN analyzer. Analysis for phosphorus was performed by spectrophotometry after oxidation of the H_2L^{2-} anion to orthophosphate. Analysis for lead was perfomed by complexometry (back titration of excess sodium ethylenediaminetetraacetate with a solution of $CuSO_4$ in the hexamethylenetetramine buffer with pH 5–6 at 60–80°C, indicator xylenol orange).

Lead(II) 1-hydroxyethane-1,1-diphosphonate(2–) monohydrate. To a solution of 2.69 g of $H_4L \cdot H_2O$ in 15 ml of water, a solution of 3.31 g of $Pb(NO_3)_2$ in 15 ml of water was added with stirring. After the primarily formed curdled precipitate had completely passed into heavy coarse crystals (5–20 days), the solvent was decanted, and the residue was washed first with 0.1 N HNO_3 and then thrice with water. The precipitate was pressed out on a paper filter and dried in air at room temperature until constant weight. Yield 97%. IR spectrum, ν, cm^{-1}: 3600–2400, 2300–2100, 1680–1640 w [δ(H_2O)], 1240, ~1200 s, 1165 s [$\nu_{as}(PO_2)$], 1090 sh, 1067 s, 1035 s [$\nu_s(PO_2)$], 945 sh, 920 s {ν[PO(H)]}, 825, 700, 658, 545 s, 488, 463, 445 s, 408. Found, %: C 5.2; H 1.6; P 14.1; Pb 48.0. $C_2H_8O_8P_2Pb$. Calculated, %: C 5.60; H 1.88, P 14.43; Pb 48.27.

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