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Protonated Sodium 1-Hydroxyethane-1,1-diphosphonates

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Abstract — Powder X-ray diffraction study of sodium salts of 1-hydroxyethane-1,1-diphosphonic acid (H_4L) of the compositions $NaH_3L \cdot H_2O$, $Na_2H_2L \cdot 4H_2O$, and $Na_3HL \cdot 5.5H_2O$ showed that these compounds are single-phase. Some of their properties were determined. The possibility of preparing salts of other compositions was examined.

Sodium 1-hydroxyethane-1,1-diphosphonates of different compositons were isolated from aqueous acetic acid and aqueous solutions [1–3]. They are used either directly as drugs (e.g., $Na_2H_2L \cdot 4H_2O$, Disodium Etidronate) or as starting substances for their preparation ($NaH_3L \cdot H_2O$ [3, 4]). The salt $Na_3HL \cdot 6H_2O$ is used in industry.

The structures of sodium 1-hydroxyethane-1,1-diphosphonates $NaH_3L \cdot H_2O$ [5,6] and $Na_2H_2L \cdot H_2O$ [7] are known.

In this work we examined the possibility of formation of protonated sodium 1-hydroxyethane-1,1-diphosphonates of other compositions. The products were identified by powder X-ray diffraction.

The crystallographic data (Table 1) obtained for single crystals of $NaH_3L \cdot H_2O$ grown from aqueous acetic acid (sample nos. 1, 2) and water (sample nos. 3, 4) coincide. The agreement of the X-ray diffraction pattern calculated from the single crystal data [5] with the experimental powder X-ray pattern of $NaH_3L \cdot H_2O$ (Table 2) shows that its polycrystalline samples are single-phase.

All the attempts to prepare the salt of the composition $NaH_7L_2 \cdot nH_2O$ failed. Slow evaporation of the aqueous solution of the composition NaH_7L_2 and also the addition of excess acetic acid yielded a crystalline precipitate which, according to powder X-ray pattern, was single-phase $NaH_3L \cdot H_2O$.

Concentration of an aqueous solution of the composition Na_2H_2L at room temperature gives a finely crystalline precipitate of $Na_2H_2L \cdot 4H_2O$ which, according to the powder X-ray pattern (Table 3), is single-phase.

Slow evaporation of an aqueous solution of the composition $Na_{1.5}H_{2.5}L$ yields a syrup without formation of a solid phase. Treatment of $Na_xH_{4-x}L$ solutions (x = 1.5–2) with excess acetic acid yields a single-phase $NaH_3L \cdot H_2O$ precipitate.

Air-dry samples of trisodium hydrogen 1-hydroxyethane-1,1-diphosphonate obtained from aqueous solution at room temperature always have the composition $Na_3HL \cdot 5.5H_2O$ [8]. Their powder X-ray patterns (Table 4) have the same set of interplanar spacings with the same reflection intensities. In combination with analytical data, this fact suggests that the substance is single-phase, although this is not an unambiguous proof.

Sodium trihydrogen 1-hydroxyethane-1,1-diphosphonate $NaH_3L \cdot H_2O$ forms colorless prismatic crystals, and $Na_2H_2L \cdot 4H_2O$ and $Na_3HL \cdot 5.5H_2O$ are finely crystalline powders. These salts are readily soluble in water (pH of 0.02 M solution 2.45, 5.00, and 8.85; concentration of saturated solution at 22°C 1.75, 1.05, and 0.450 M, respectively), soluble in glycerol and ethylene glycol (on heating), and poorly soluble in DMSO, DMF, ethanol, 2-propanol, ethyl acetate, acetone, dioxane, chloroform, carbon tetrachloride, hexane, and benzene. Contrary to the two other salts, $NaH_3L \cdot H_2O$ is poorly soluble in acetic acid. These salts are not hygroscopic and do not lose

Table 1. Unit cell parameters of sodium trihydrogen 1-hydroxyethane-1,1-diphosphonate (space group *Pbca*, *Z* 8).

Sample no.	*a*, Å	*b*, Å	*c*, Å	References
1	7.5011(8)	11.841(1)	18.782(2)	[3][a]
2	7.499(3)	11.830(5)	18.779(6)	[5]
3	7.500(3)	11.834(4)	18.773(3)	[6]
4	7.502(3)	11.835(5)	18.779(8)	[b]

Data of: [a] O.P. Gladkikh and [b] G.G. Aleksandrov.

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Table 2. Powder X-ray diffraction pattern of sodium trihydrogen 1-hydroxyethane-1,1-diphosphonate monohydrate[a]

d, Å		*I*, %		*h k l*	*d*, Å		*I*, %		*h k l*
experiment	calculation	experiment	calculation		experiment	calculation	experiment	calculation	
9.39	9.390	48	22	0 0 2	2.254	2.254	3	7	2 4 2
	6.002		2	1 1 1	2.237	2.236	3	3	3 2 2
	5.915		35	0 2 0	2.224	2.226	2	1.7	2 2 6
5.88	5.860	45	69	1 0 2	2.206	2.206	8	14	3 0 4
5.65	5.642	35	57	0 2 1	2.178	2.177	2	2	2 4 3
5.17		5			2.161	2.161	6	12	3 2 3
4.996	5.005	4	3	0 2 2	2.145	2.146	3	4	2 1 7
4.695	4.695	100	94	0 0 4	2.127	2.127	1.5	1.7	1 3 7
4.505	4.508	6	6	1 2 1	2.094	2.098	1.3	0.9	3 3 1
4.452	4.452	5	1.5	1 1 3		2.095		0.7	1 2 8
4.302	4.299	68	100	0 2 3	2.080	2.081	1.2	2	2 4 4
4.158	4.163	4	5	1 2 2		2.067		2	3 2 4
3.766	3.772	4	3	1 1 4	2.066	2.066	4	3	1 4 6
3.745	3.750	4	7	2 0 0		2.060		3	3 3 2
3.679	3.677	1.8	1.6	0 2 4		2.052		1	2 3 6
3.499	3.511	2	1	2 1 1	2.046	2.047	1.5	1.7	2 2 7
3.479	3.482	5	9	2 0 2	2.033	2.034	1.5	2	1 5 4
3.271	3.273	2	3	1 3 2	2.001	2.001	0.9	1.3	3 3 3
3.230	3.231	6	5	1 1 5		1.990		1.2	2 5 1
3.170	3.171	5	4	0 2 5	1.989	1.990	10	7	2 0 8
	3.130		14	0 0 6	1.967	1.968	7	6	0 2 9
3.125	3.123	75	100	2 2 1		1.961		1.5	0 6 1
3.049	3.048	4	5	1 3 3	1.948	1.953	4	3	3 0 6
2.998	3.001	4	6	2 2 2		1.948		4	1 3 8
2.958	2.958	4	5	0 4 0		1.934		1.4	1 5 5
2.930	2.930	30	32	2 0 4	1.927	1.926	1.6	2	3 3 4
	2.922		17	0 4 1	1.903	1.909	5	4	2 3 7
2.840	2.844	6	10	2 1 4		1.903		3	1 2 9
2.825	2.826	5	6	2 2 3	1.880	1.881	2	3	0 6 3
	2.821		3	0 4 2		1.875		2	4 0 0
2.799	2.801	4	5	1 3 4		1.869		1.1	1 6 2
2.767	2.766	14	14	0 2 6	1.866	1.865	5	7	2 4 6
2.718	2.722	2	4	1 4 1	1.839	1.843	1.8	2	4 1 1
2.685	2.689	2	5	2 3 1		1.824		1.6	1 6 3
2.634	2.640	0.9	1.3	1 4 2	1.819	1.818	3	3	0 6 4
2.608	2.610	6	12	2 3 2		1.817		1.7	4 1 2
2.595	2.595	9	7	1 2 6	1.800	1.800	1.2	0.9	1 1 10
	2.589		1.2	2 1 5	1.747	1.747	5	4	3 2 7
2.556	2.557	1.0	1.8	1 3 5		1.746		1.4	0 6 5
2.501	2.502	1.0	1.2	0 4 4		1.745		2	2 6 0
2.469	2.470	2	2	1 1 7	1.700	1.700	1.3	2	1 6 5
2.443	2.443	12	11	0 2 7	1.680	1.679	1.7	1.8	2 0 10
2.421	2.421	17	22	2 2 5	1.663	1.662	1.2	1.1	2 1 10
	2.416		2	3 0 2	1.651	1.651	3	4	2 4 8
2.403	2.403	3	3	2 0 6		1.636		1.2	2 6 4
2.365	2.367	1.5	3	3 1 2	1.629	1.630	4	4	3 4 6
2.346	2.347	4	1.5	0 0 8		1.627		2	1 5 8

Table 2. (Contd.)

d, Å		*I*, %		*h k l*	*d*, Å		*I*, %		*h k l*
experiment	calculation	experiment	calculation		experiment	calculation	experiment	calculation	
	2.324		1.7	0 4 5		1.624		1.0	1 7 2
2.322	2.323	5	4	1 2 7	1.615	1.615	2	1.1	2 2 10
	2.322		1.5	2 4 0	1.589	1.589	1.2	1.0	0 6 7
2.281	2.285	0.8	1.0	3 2 1					

[a] The interplanar spacings (*d*) corresponding to the reflections with the relative intensity $I > 1\%$ are given. The experimental intenities were evaluated from the peak heights in the powder X-ray pattern, and the calculated intensities, from the intergal intensities of reflections.

Table 3. Powder X-ray diffraction pattern of sodium dihydrogen 1-hydroxyethane-1,1-diphosphonate tetrahydrate[a]

d, Å		*I*, %		*h k l*	*d*, Å		*I*, %		*h k l*
experiment	calculation	experiment	calculation		experiment	calculation	experiment	calculation	
10.60	10.593	100	100	1 0 0	2.577	2.576	12	15	2 2 1
7.02	7.022	24	18	$\bar{1}$ 0 2	2.564	2.563	11	7	$\bar{3}$ 1 4
6.80	6.811	99	72	1 0 2	2.505	2.505	6	3	0 2 4
5.70	5.694	15	24	0 1 1		2.428		4	1 2 4
5.30	5.297	68	30	2 0 0	2.422	2.422	18	9	4 1 0
5.22	5.216	16	17	1 1 0		2.410		9	$\bar{2}$ 2 3
	5.036		30	$\bar{1}$ 1 1	2.338	2.341	9	2	$\bar{3}$ 0 6
5.02	5.010	27	3	0 1 2		2.325		3	4 1 2
	4.995		27	1 1 1	2.320	2.322	30	7	$\bar{4}$ 0 4
4.639	4.644	8	1.7	$\bar{2}$ 0 2		2.318		6	1 1 7
4.559	4.559	9	6	$\bar{1}$ 1 2	2.262	2.261	11	6	3 2 1
3.893	3.897	8	4	$\bar{2}$ 1 1	2.226	2.229	3	2	4 1 3
3.862	3.860	9	5	2 1 1	2.217	2.217	7	3	1 0 8
	3.631		3	0 1 4	2.179	2.180	10	5	$\bar{3}$ 1 6
3.609	3.609	10	9	2 1 2	2.163	2.165	6	1.3	$\bar{4}$ 1 4
3.527	3.531	12	4	3 0 0	2.114	2.115	6	2	4 1 4
3.458	3.461	8	6	$\bar{1}$ 1 4	2.077	2.079	11	3	1 1 8
3.406	3.409	11	8	1 1 4		2.050		2	5 0 2
3.357	3.360	7	3	$\bar{2}$ 1 3	2.045	2.045	13	5	$\bar{4}$ 1 5
3.285	3.289	7	5	2 1 3	2.025	2.029	3	1.6	$\bar{4}$ 0 6
3.259	3.259	17	6	3 0 2	2.005	2.006	5	1.8	$\bar{3}$ 1 7
3.116	3.118	7	4	0 1 5	1.966	1.967	5	1.7	0 2 7
3.027	3.030	29	19	$\bar{2}$ 1 4	1.942	1.945	8	1.3	$\bar{5}$ 0 4
	3.013		17	1 1 5		1.940		2	5 1 2
	2.997		2	0 2 0		1.922		1.5	$\bar{4}$ 1 6
	2.970		3	1 1 5	1.921	1.921	7	1.4	0 1 9
2.961	2.961	17	5	2 1 4		1.920		1.5	3 2 5
	2.957		13	0 2 1	1.858	1.857	4	2	2 3 1
	2.909		7	$\bar{3}$ 1 2	1.827	1.827	2	1.3	2 3 2
2.899	2.900	61	30	1 0 6	1.805	1.807	2	1.0	$\bar{1}$ 3 4
	2.883		8	1 2 0	1.786	1.789	3	1.8	2 1 9

Table 3. (Contd.)

d, Å		*I*, %		*h k l*	*d*, Å		*I*, %		*h k l*
experiment	calculation	experiment	calculation		experiment	calculation	experiment	calculation	
2.862	2.863	14	8	3 1 2	1.781	1.781	3	2	2 3 3
	2.847		2	0 2 2	1.741	1.742	16	7	$\bar{2}$ 0 10
2.834	2.835	54	25	$\bar{3}$ 0 4		1.739		4	3 3 0
2.751	2.752	37	19	3 0 4		1.726		2	$\bar{5}$ 2 1
	2.718		6	$\bar{2}$ 1 5	1.702	1.703	10	3	4 0 8
2.713	2.713	26	18	0 1 6		1.702		4	3 2 7
2.684	2.688	6	4	0 2 3	1.675	1.675	6	3	$\bar{5}$ 2 3
	2.656		2	2 1 5	1.586	1.586	4	1.2	4 3 1
2.649	2.648	13	3	4 0 0	1.562	1.562	5	4	4 2 7
	2.611		3	1 1 6					
2.603	2.603	17	4	2 0 6					
	2.597		11	1 2 3					

[a] The interplanar spacings (*d*) corresponding to the reflections with I_{exp} or I_{calc} > 2% are presented. The experimental intensities were evaluated from the peak heights in the powder X-ray pattern, and the calculated intensities, from the integral intensities of reflections.

Table 4. Interplanar spacings (*d*) and relative intensities of reflections (*I*) in the powder X-ray pattern of trisodium hydrogen 1-hydroxyethane-1,1-diphosphonate 5.5-hydrate[a]

d, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %
12.22	100	3.461	4	2.397	2	1.999	2
8.76	1.7	3.432	4	2.374	16	1.982	3
7.96	10	3.413	4	2.354	7	1.969	3
6.48	27	3.377	3	2.342	4	1.946	1.2
6.13	24	3.137	6	2.332	2	1.922	4
5.62	25	3.117	2	2.300	4	1.877	1.0
4.955	3	3.042	19	2.277	2	1.859	1.3
4.821	11	2.988	7	2.256	8	1.823	1.0
4.720	1.3	2.916	25	2.250	8	1.800	4
4.574	9	2.889	5	2.241	8	1.766	1.0
4.503	11	2.818	32	2.181	1.0	1.753	3
4.429	3	2.711	34	2.166	2	1.734	1.0
4.094	10	2.658	11	2.138	2	1.708	1.5
4.018	8	2.626	1.3	2.119	1.2	1.686	2
3.846	5	2.534	6	2.108	1.2	1.638	2
3.800	1.3	2.508	1.2	2.094	0.8	1.539	1.5
3.584	1.7	2.487	7	2.059	3	1.394	2
3.505	3	2.460	4	2.014	5		

[a] The interplanar spacings corresponding to the reflections with *I* > 1% are given.

water of crystallization when handled in air at room temperature.

EXPERIMENTAL

Sodium 1-hydroxyethane-1,1-diphosphonates were prepared as described in [2, 3].

Powder X-ray diffraction patterns were obtained on a DRON-3 diffractometer (CuK_α radiation, graphite monochromator, external reference α-Al_2O_3, 2θ 3°–60°). To evaluate the solubility of salts, their powders were stirred with water until the constant concentration in solution was attained. The concentrations of $H_nL^{(4-n)-}$ anions in the filtrate were evaluated according to [8].

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