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Dimethylammonium Trihydrogen 1-Hydroxyethane-1,1-diphosphonate

E. G. Afonin and G. G. Aleksandrov

Laboratory of Chemical Engineering, State Enterprise, Kaluga, Russia
Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia

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Abstract—Dimethylammonium trihydrogen 1-hydroxyethane-1,1-diphosphonate $(CH_3)_2NH_2(H_3L) \cdot H_2O$ was prepared. Powder X-ray diffraction study showed that the polycrystalline product is single-phase. The thermal transformations of the compound were studied. The crystalline anhydrous salt was prepared by thermal dehydration of the monohydrate.

Addition of dimethylamine in 1:1 molar ratio to an aqueous acetic acid solution containing 1-hydroxyethane-1,1-diphosphonic acid $CH_3C(OH)(PO_3H_2)_2$ (H_4L), followed by addition of ethanol, causes precipitation of monoclinic crystals of dimethylammonium trihydrogen 1-hydroxyethane-1,1-diphosphonate $(CH_3)_2NH_2(H_3L) \cdot H_2O$, a 16.834(1), b 8.147(1), c 8.603(2) Å, β 93.42(4)°, $Z = 4$, space group $P2_1/n$ [1].

The salt of the same composition crystallizes on adding ethanol to a concentrated aqueous solution of $(CH_3)_2NH_2(H_3L) \cdot H_2O$ containing a 10% excess of H_4L. The X-ray pattern calculated from the single crystal X-ray diffraction data for $(CH_3)_2NH_2(H_3L) \cdot H_2O$ [1] and the experimental powder X-ray pattern of this compound are in good agreement (Table 1), which, in combination with the analytical data, shows that the polycrystalline product is single-phase.

The salt $(CH_3)_2NH_2(H_3L) \cdot H_2O$ was obtained as colorless prismatic crystals and concretions. This compound is highly soluble in water (pH of 0.02 M solution 2.45), soluble in acetic acid, DMSO, DMF, and glycerol, and poorly soluble in ethanol, isopropanol, ethyl acetate, acetone, dioxane, chloroform, carbon tetrachloride, hexane, and benzene. The compound is weakly hygroscopic, it does not loose water of crystallization when handled in air at room temperature.

The derivatogram (see figure) gives the general information about thermal transformations of $(CH_3)_2 \cdot NH_2(H_3L) \cdot H_2O$. Dehydration starts at 55°C and is accompanied by melting in water of crystallization (DTA$_{min}$ 80°C), which causes a sharp decrease in the dehydration rate. Heating of the monohydrate first at 70 and then at 110°C to constant weight (3–5 h) allows preparation of the crystalline anhydrous salt (Table 2), avoiding the complications arising from formation of a melt (weight loss: found 6.7%, calculated 6.69%; $C_2H_4O_7P_2^{4-}$ content: found 80.1%, calculated 80.44%). $(CH_3)_2NH_2(H_3L)$ melts at 160°C and starts to decompose at 170°C with the cleavage of the P–C bond in the H_3L^- anion (DTA$_{min}$ 200–220°C), which is mainly due to the interaction of $(CH_3)_2NH_2^+$ and H_3L^-, rather than to the thermal lability of the anion. Further heating is accompanied by abundant evolution of gaseous products (see figure), with a series of exothermic (DTA$_{max}$ 240°C) and endothermic effects.

EXPERIMENTAL

The salt was prepared from a solution obtained by dilution with water of 33% dimethylamine solution (chemically pure grade) and $H_4L \cdot H_2O$ purified by recrystallization of the pure grade reagent from 80% acetic acid. The powder X-ray diffraction patterns were obtained on a DRON-3 diffractometer (CuK_α radiation, graphite monochromator, 2θ 3°–60°). The IR spectrum of the salt (KBr pellet) was recorded on a UR-20 spectrometer in the range 4000–400 cm^{-1}. The derivatogram was measured on an OD-103 derivatograph (quartz crucible, 50 mg sample) under nitrogen; the heating rate was 6 deg/min in the range 20–600°C. The content of the 1-hydroxyethane-1,1-diphosphonate anion in salts was determined according to [2]. Decomposition of the anion on heating of the salt was studied similarly to [3].

Dimethylammonium trihydrogen 1-hydroxyethane-1,1-diphosphonate monohydrate. To a solution of 2.46 g of H_4L in 10 ml of water, 5 ml of a 2 M solution of dimethylamine was added with stirring. The resulting solution was evaporated on a water bath

Table 1. Powder X-ray diffraction pattern of dimethylammonium 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	
8.40	8.402	9	9	2 0 0	2.646	2.649	8	8	6 1 0
7.84	7.839	8	9	$\bar{1}$ 0 1	2.614	2.614	7	4	$\bar{2}$ 1 3
7.46	7.469	60	61	1 0 1		2.613		4	$\bar{3}$ 0 3
7.34	7.331	100	100	1 1 0	2.591	2.592	10	7	5 2 0
5.90	5.910	3	3	0 1 1		2.589		1.7	0 3 1
5.65	5.649	11	15	$\bar{1}$ 1 1	2.566	2.566	3	1.5	$\bar{1}$ 3 1
5.50	5.505	3	3	1 1 1		2.492		1.6	6 1 1
4.931	4.930	17	20	$\bar{2}$ 1 1	2.486	2.488	5	3	$\bar{3}$ 1 3
4.819	4.825	14	20	$\bar{3}$ 0 1	2.464	2.465	2	1.4	$\bar{4}$ 2 2
4.742	4.743	1.7	1.2	2 1 1	2.448	2.454	3	3	5 1 2
4.615	4.616	1.7	1.1	3 1 0		2.444		1.5	3 3 0
4.568	4.569	1.7	1.7	3 0 1	2.378	2.381	0.7	1.0	3 1 3
4.295	4.294	5	6	0 0 2	2.369	2.367	1.0	1.0	$\bar{3}$ 3 1
4.199	4.201	5	4	4 0 0	2.334	2.335	3	4	$\bar{1}$ 2 3
4.154	4.152	7	10	$\bar{3}$ 1 1		2.303		1.0	7 1 0
3.985	3.985	17	19	3 1 1	2.295	2.295	3	4	0 3 2
	3.959		1.4	1 2 0	2.276	2.277	2	1.4	7 0 1
3.797	3.799	14	18	0 1 2	2.264	2.264	2	1.9	1 3 2
3.737	3.748	11	10	$\bar{1}$ 1 2	2.229	2.232	1.5	1.2	$\bar{2}$ 3 2
	3.734		5	2 0 2		2.228		1.3	2 2 3
	3.734		3	4 1 0	2.200	2.199	1.5	1.2	6 1 2
3.670	3.680	9	5	0 2 1	2.147	2.147	1.5	1.9	0 0 4
	3.665		5	2 2 0	2.100	2.101	1.6	1.2	8 0 0
3.614	3.615	6	8	$\bar{1}$ 2 1	2.068	2.068	2	2	7 2 0
3.574	3.576	1.3	1.2	1 2 1	2.033	2.035	0.8	0.8	$\bar{7}$ 2 1
3.527	3.532	0.9	0.4	$\bar{2}$ 1 2	1.986	1.988	0.5	0.6	4 3 2
3.492	3.493	1.3	1.5	$\bar{4}$ 1 1	1.965	1.965	1.5	0.7	1 4 1
	3.403		0.9	$\bar{2}$ 2 1	1.951	1.954	2	1.9	8 1 1
3.392	3.395	7	8	2 1 2		1.950		1.1	6 3 0
	3.360		1.9	4 1 1		1.905		1.3	$\bar{4}$ 1 4
3.340	3.340	10	10	2 2 1	1.898	1.901	3	1.0	2 3 3
3.224	3.224	1.9	3	$\bar{3}$ 1 2		1.899		1.2	0 2 4
	3.113		3	$\bar{3}$ 2 1	1.802	1.802	3	1.2	$\bar{9}$ 1 1
3.105	3.107	17	14	5 1 0	1.756	1.762	0.5	1.0	$\bar{3}$ 4 2
3.039	3.040	6	6	3 2 1	1.747	1.748	0.4	0.7	6 3 2
2.972	2.975	1.1	1.0	$\bar{5}$ 1 1	1.718	1.719	0.3	0.7	$\bar{7}$ 2 3
2.953	2.955	2	1.9	0 2 2	1.680	1.682	1.5	1.4	$\bar{1}$ 1 5
2.917	2.917	3	2	4 0 2	1.668	1.668	1.0	0.4	1 3 4
	2.895		5	$\bar{4}$ 1 2		1.667		0.3	$\bar{2}$ 1 5
2.889	2.890	13	11	1 2 2	1.639		0.7		
2.871	2.871	3	2	5 1 1	1.632	1.633	0.8	0.9	7 3 2
2.849	2.850	1.7	3	$\bar{1}$ 0 3	1.615	1.618	0.8	0.9	2 4 3
2.798	2.801	3	2	6 0 0	1.597	1.597	0.6	0.5	5 4 2
2.752	2.753	6	7	2 2 2	1.566		0.4		
2.681	2.681	3	3	1 3 0					

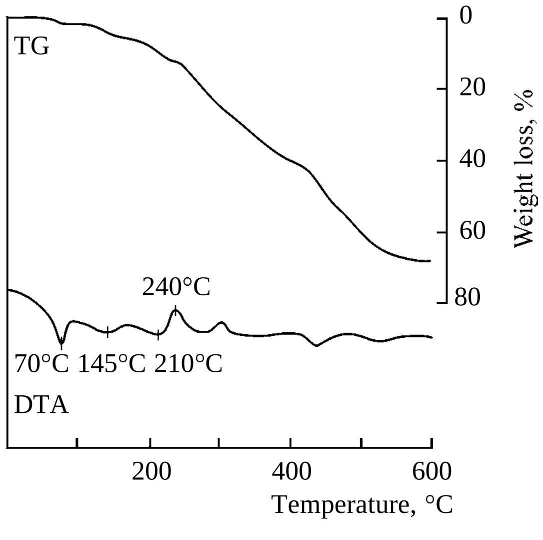
[a] Interplanar spacings (*d*) corresponding to reflections with relative intensities $I_{exp} > 0.5\%$ are given. The experimental intensities were evaluated from the peak heights in the powder X-ray pattern, and the calculated intensities, from the integral intensities of reflections.

Table 2. Interplanar spacings (*d*) and relative intensities of reflections (*I*) in the powder X-ray diffraction pattern of anhydrous dimethylammonium trihydrogen 1-hydroxyethane-1,1-diphosphonate[a]

d, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %	*d*, Å	*I*, %
9.03	12	3.453	43	2.436	5	1.968	2
7.83	100	3.264	27	2.417	12	1.952	3
6.86	53	3.241	26	2.408	12	1.932	3
6.52	86	3.143	20	2.379	2	1.898	1.5
6.26	47	3.098	5	2.329	12	1.850	1.5
6.18	25	3.044	22	2.317	7	1.780	2
5.59	17	3.022	17	2.276	2	1.755	1.5
5.03	12	2.959	3	2.265	4	1.721	3
4.801	1.9	2.948	2	2.250	4	1.706	1.5
4.529	37	2.877	3	2.220	3	1.677	2
4.461	71	2.802	11	2.199	4	1.647	1.5
4.418	16	2.719	6	2.191	4	1.613	1.5
4.152	10	2.667	8	2.113	1.5	1.584	1.5
4.110	37	2.604	21	2.097	3	1.578	1.5
3.969	10	2.564	5	2.079	1.5	1.560	1.5
3.860	5	2.516	12	2.065	3	1.526	1
3.779	33	2.503	16	2.006	3	1.518	1
3.702	27	2.468	4	1.985	6	1.502	1

[a] Only *d* values corresponding to the reflections with $I > 1\%$ are given.

to a volume of 3 ml, and 30 ml of ethanol was added with stirring. The liquid separated into layers. After complete crystallization of the lower layer, the solution was decanted and the crystals were washed first with 70% aqueous ethanol and then with pure ethanol, pressed out on a paper filter, and dried in air at room temperature to constant weight. IR spectrum, %: 3500–3440, 3260–3140, 3070–3010, 2860–2800, ~2485, ~2310, 1750–1700, 1650–1635, 1485, 1460–1425, 1290–1275, 1180, 1125 sh, 1105, 1080 sh, 1025 sh, 1010, 990 sh, 935, 900, 642, 569, 550, 515, 480–465, 455, 420 sh. Found, %: C 17.5; H 6.5; N 5.4; P 22.7; $C_2H_4O_7P_2^{4-}$ 75.0. $C_4H_{17}NO_8P_2$. Calculated, %: C 17.85; H 6.37; N 5.20; P 23.02; $C_2H_4O_7P_2^{4-}$ 75.05.



Derivatogram of $(CH_3)_2NH_2(H_3L)\cdot H_2O$.

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