

BASIC CRYSTALLOGRAPHIC DATA OF ANHYDROUS HEXAAMIDOCYCLOTRIPHOSPHAZENE AND ITS MONOHYDRATE

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Powder photographs of $(\text{PN}(\text{NH}_2)_2)_3$ and $(\text{PN}(\text{NH}_2)_2)_3 \cdot \text{H}_2\text{O}$ were indexed based on the lattice parameters obtained from the single crystal data, and the parameters were refined by using the least-squares method. The space groups belonging to the two crystalline substances are *Pbca* ($Z = 8$) and *P1* ($P1$) ($Z = 2$), respectively.

Hexaamidocyclotriphosphazene $(\text{PN}(\text{NH}_2)_2)_3$ (HACTP) was first prepared by Besson and Rosset¹ by prolonged action of liquid ammonia on $(\text{PNCl}_2)_3$ in a sealed tube. Since then, the preparation of HACTP was multiply verified and the procedure modified in a variety of ways.

Hexaamidocyclotriphosphazene monohydrate $(\text{PN}(\text{NH}_2)_2)_3 \cdot \text{H}_2\text{O}$ (HACTP.H₂O) was prepared by Moureu and Rocquet² by precipitation of HACTP aqueous solution with ethanol. Other authors, however, were unable to confirm the existence of the monohydrate, and it was not until 1970 that the existence was proved by Wakenfield, Luff and Kohler³.

In the present work, single crystals of the two substances, HACTP and HACTP.H₂O, were prepared and their basic crystallographic data were determined.

EXPERIMENTAL

X-Ray Diffraction Study

The single crystals were fixed to glass fibres and protected against atmospheric humidity by a varnish layer, the powder samples were sealed in quartz capillaries 0.3 mm in diameter. Precision photographs were obtained on a PDK-1 camera (Dioptra, Kroměříž), the Weissenberg photographs were obtained on a Nonius goniometer using Ni-filtered CuK_α radiation, $\lambda = 154.178$ pm. The powder photographs were taken in a Debye-Scherrer camera 114.6 mm in diameter (Freiberger Präzisionsmechanik, GDR) applying an asymmetric self-calibrating Straumanis film position with CrK_α radiation, $\lambda = 229.092$ pm. The line positions were measured on a precision Abbe comparator (Zeiss, Jena) and the intensities of the diffraction lines were estimated in a 1–10 scale.

Preparation of the Crystals

Anhydrous HACTP single crystals were prepared by slow ammonolysis of $(\text{PNCl}_2)_3$ by liquid ammonia. Approximately 1 g of chlorophosphazene was placed in a glass tube with volume about 200 ml, and the tube was submerged in EtOH-dry ice cooling mixture.

An access of atmospheric humidity during the procedure was prevented by feeding dry nitrogen through a side inlet situated in the neck of the tube. After perfect cooling of the ampoule, 100 to 150 ml of liquid ammonia was condensed in it. The ampoule was sealed off and allowed to reach slowly the ambient temperature; this took 24–48 h, according to the quality of the Dewar flask used. In the first stage, $(\text{PNCl}_2)_3$ dissolved partially in cool ammonia without apparent reaction; subsequently, the substance was ammonolyzed during the slow heating, and HACTP crystallized in the ampoule in the shape of up to several centimeters long needles.

If, however, the tube was removed from the cooling mixture immediately after the sealing, a fast reaction occurred during the heating, giving rise to a very fine product, unsuitable for X-ray diffraction analysis.

TABLE I
Powder diagram of hexaamidocyclotriphosphazene

d_{obs}^a	d_{calc}^a	hkl	I/I_0	d_{obs}	d_{calc}^a	hkl	I/I_0
715.8	712.1	111	10	217.2	217.5	600	1
645.7	652.4	200	4	215.6	215.6	250	1
574.3	571.7	102	3	211.1	210.7	611	1
516.5	517.5	211	1	207.8	208.8	343	1
424.4	424.9	022	2	204.8	205.0	325	1
404.9	404.0	122	1	202.5	202.5	612	1
385.6	387.2	311	8	198.8	198.7	514	1
356.1	356.1	222	2	191.6	191.6	443	1
349.4	351.3	131	2	180.9	180.9	261	1
341.0	340.4	023	1	178.7	178.9	702	1
326.5	328.8	230	1	157.2	157.2	417	1
322.9	326.2	400	1	150.6	150.5	616	1
319.8	318.3	231	4	147.6	147.6	653	1
316.0	316.9	132	5	142.0	141.9	081	1
291.6	292.1	232	1	139.9	139.8	735	1
287.3	285.6	204	1	131.8	13.18	139	1
281.3	281.3	412	1	130.9	131.0	375	1
260.5	260.5	042	1	128.9	128.9	419	1
256.7	256.7	304	1	125.7	125.7	746	1
238.6	239.9	134	1	124.1	124.1	2, 1, 10	1
222.9	222.6	243	1				

^a Interplanar spacing in pm.

TABLE II
Powder diagram of hexaamidocyclotriphosphazene monohydrate

d_{obs}^a	d_{calc}^a	hkl	I/I_0	d_{obs}^a	d_{calc}^a	hkl	I/I_0
829.5	819.9	001	8	248.7	249.1	$2\bar{1}\bar{2}$	1
729.2	707.9	010	6	245.5	244.3	$\bar{3}22$	1
697.7	696.0	$1\bar{1}0$	6	232.2	232.0	$\bar{3}31$	1
661.3	661.2	$\bar{1}00$	6	228.5	228.6	$\bar{3}02$	1
608.5	603.7	01 $\bar{1}$	8	221.1	221.3	$3\bar{1}\bar{3}$	1
577.6	572.0	$\bar{1}11$	6	217.5	217.4	$\bar{1}04$	1
495.2	497.1	$\bar{1}1\bar{1}$	1	206.2	206.1	$\bar{2}\bar{2}1$	1
454.4	446.8	101	1	202.7	202.8	$\bar{2}\bar{4}1$	1
413.7	414.1	$\bar{1}20$	5	200.4	200.6	$\bar{4}21$	1
393.8	393.2	$2\bar{1}\bar{1}$	6	198.2	198.6	$1\bar{4}0$	1
378.3	377.3	$1\bar{1}\bar{2}$	6	196.5	196.5	$3\bar{4}0$	1
359.8	363.6	$\bar{1}21$	5	191.4	191.4	$\bar{4}12$	1
350.0	349.8	$\bar{2}01$	1	155.2	155.2	$3\bar{4}3$	1
345.3	342.9	$\bar{1}\bar{1}2$	3	152.5	152.5	$\bar{5}41$	1
339.4	338.0	$2\bar{2}\bar{1}$	5	149.3	149.3	$4\bar{5}1$	1
331.5	330.5	$\bar{2}00$	10	138.0	138.0	$3\bar{6}0$	1
316.1	316.8	111	1	133.8	133.8	$2\bar{2}\bar{6}$	1
310.0	313.7	$20\bar{2}$	1	127.8	127.8	$1\bar{3}6$	1
303.8	305.2	$2\bar{2}1$	1	125.6	125.5	$\bar{6}51$	1
275.8	276.2	201	1	119.5	119.5	$4\bar{6}3$	1
271.0	271.3	$\bar{1}30$	1	118.5	118.5	$2\bar{2}7$	1
261.2	260.8	$\bar{1}20$	1	115.0	115.0	242	1
255.4	256.0	$\bar{3}20$	1				

^a Interplanar spacing in pm.

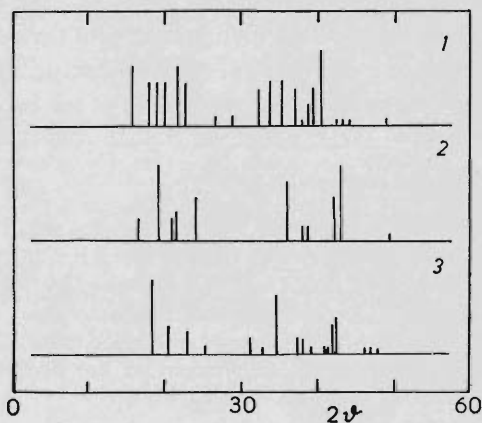


FIG. 1

Line diagrams of hexaamidocyclotriphosphatene monohydrate 1, 2 and of anhydrous hexaamidocyclotriphosphatene 3. 1, 3 Our measurements, 2 ref.⁶

Hexamidocyclotriphosphazene monohydrate single crystals were prepared by slow cooling of aqueous solution of HACTP, concentration about 0.3 g in 5 ml of water, down to 0°C. In view of the fact that the hydrate is prone to weathering on air and at temperature above 20°C it undergoes a so far unidentified transformation³, the crystals were isolated at temperatures near 5°C only just before use, and the X-ray diffraction photographs were taken at temperatures not exceeding 15°C.

RESULTS

The diffraction symmetry of HACTP single crystals is $2/m\ 2/m\ 2/m$, and the systematic extinctions determine unambiguously space group $Pbca$, $Z = 8$. The lattice parameters were obtained from the indexed powder photograph, applying the refinement procedure of the LATTREF program, our adapted version⁴ of the MPEXT-6 program. The values obtained are $a = 1304.8(7)$, $b = 1142.1(5)$, $c = 1272.0(4)$ pm, $V = 1.8956\text{ nm}^3$, $D_m = 1.68\text{ g cm}^{-3}$, $D_x = 1.61\text{ g cm}^{-3}$. The indexed powder diagram is presented in Table I. The density of HACTP was taken from ref.⁵.

HACTP.H₂O crystallizes in regular parallelepipeds with apparent triclinic symmetry. No physical tests for the occurrence of the centre of symmetry were undertaken, and the suggestion of centrosymmetric space group $P\bar{1}$ is based on an even number of formula units ($Z = 2$) in a unit cell.

The density of the crystals was determined by the floating method in a methylene iodide-benzene mixture. The crystallographic data obtained are $a = 803(1)$ pm, $b = 829(1)$ pm, $c = 871(1)$ pm, $\alpha = 95.3(1)^\circ$, $\beta = 106.8(1)^\circ$, $\gamma = 119.50(3)^\circ$, $V = 0.4635\text{ nm}^3$, space group $P\bar{1}(P1)$, $Z = 2$, $D_m = 1.70\text{ g cm}^{-3}$, $D_x = 1.73\text{ g cm}^{-3}$. The indexed powder diagram is presented in Table II. The powder diagram of the substance has been published by Kobayashi⁶, but as the line diagrams demonstrate (Fig. 1), the product was obviously partly decomposed.

Despite the fact that the samples were prepared with care, the diffraction lines of the powder photographs are diffuse and generally weak. For this reason, use could not be made of the high precision of the comparator, and the errors in the line positions are more random than systematic. In view of this, no extrapolation function was employed for the refinement of the lattice parameters.

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