

References

- B. A. FRENZ & ASSOCIATES, INC. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.
- BICHSEL, R., LEVY, F. & BERGER, H. (1984). *J. Phys. C*, **17**, L19–L21.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- BÖTTCHER, P. (1979). *J. Less Common Met.* **63**, 99–103.
- ELLIOT, N. (1960). *J. Chem. Phys.* **33**, 903–905.
- EZZAOULA, H., HEINDL, R. & LORIER, J. (1984). *J. Mat. Sci. Lett.* **3**, 625–626.
- FLAMM, W. (1986). Thesis, RWTH Aachen, Federal Republic of Germany.
- GABE, E. J., LEE, F. L. & LE PAGE, Y. (1985). *The NRCVAX Crystal Structure System*. In *Crystallographic Computing 3*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 167–174. Oxford: Clarendon Press.
- International Tables for X-ray Crystallography* (1972). Vol. II. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- LUTZ, H. D., JUNG, M. & WÄSCHENBACH, G. (1987). *Z. Anorg. Allg. Chem.* **554**, 87–91.
- MÜLLER, B. (1990). Thesis, Univ. Siegen, Federal Republic of Germany.
- STASSEN, W. N. & HEYDING, R. D. (1968). *Can. J. Chem.* **46**, 2159–2163.
- SUTARNO, KNOP, O. & REID, K. I. G. (1967). *Can. J. Chem.* **45**, 1391–1399.
- VAN VECHTEN, J. A. & PHILLIPS, J. C. (1970). *Phys. Rev. B*, **2**, 2160–2167.
- WEBER, K. (1969). *Acta Cryst.* **B25**, 1174–1178.

Acta Cryst. (1990). **C46**, 2005–2007

Crystal Chemistry of *cyclo*-Hexaphosphates. XII. Structure of Ammonium Calcium *cyclo*-Hexaphosphate Hexahydrate

BY M. T. AVERBUCH-POUCHOT

Laboratoire de cristallographie, associé à l'Université J. Fourier, CNRS, 166X, 38042 Grenoble CEDEX, France

(Received 8 December 1989; accepted 26 February 1990)

Abstract. $\text{Ca}_2(\text{NH}_4)_2\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$, $M_r = 698\cdot 154$, orthorhombic, $P2_12_12$, $a = 12\cdot 821$, $b = 12\cdot 537$ (6), $c = 7\cdot 029$ (2) Å, $V = 1130$ (1) Å³, $Z = 2$, $D_x = 2\cdot 052$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0\cdot 7107$ Å, $\mu = 1\cdot 021$ mm⁻¹, $F(000) = 712$, $T = 294$ K, final $R = 0\cdot 035$ for 1667 reflections. This compound is the first reported example of a P_6O_{18} ring anion with twofold internal symmetry. The P_6O_{18} ring anions and one of the ammonium groups alternate along the twofold axis, parallel to the *c* direction. The second ammonium group, also located on a binary axis, and the Ca atoms interconnect these rows.

Introduction. This work is part of a systematic investigation of monovalent–divalent cation *cyclo*-hexaphosphates. Several structure types have already been described for such compounds: $\text{Mn}_2\text{Li}_2\text{P}_6\text{O}_{18}\cdot 10\text{H}_2\text{O}$ (Averbuch-Pouchot, 1989), $\text{Cd}_2\text{Na}_2\text{P}_6\text{O}_{18}\cdot 14\text{H}_2\text{O}$ (Averbuch-Pouchot, 1990), $\text{Ca}_2\text{Li}_2\text{P}_6\text{O}_{18}\cdot 8\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1990*a*), $\text{Cu}_2(\text{NH}_4)_2\text{P}_6\text{O}_{18}\cdot 8\text{H}_2\text{O}$ (Averbuch-Pouchot & Durif, 1990*b*). $\text{Ca}_2(\text{NH}_4)_2\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$, described in the present work, is the fifth structure type observed so far in this area of *cyclo*-hexaphosphate chemistry.

Experimental. Single crystals of the title compound were prepared by adding solid gypsum to an aqueous

solution of ammonium *cyclo*-hexaphosphate at room temperature. After some days, large orthorhombic prisms of $\text{Ca}_2(\text{NH}_4)_2\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ appear in the solution.

Crystal size: $0\cdot 26 \times 0\cdot 16 \times 0\cdot 19$ mm. Density not measured. Philips PW1100 diffractometer, graphite monochromator. 17 reflections ($11\cdot 0 < \theta < 13\cdot 0^\circ$) for refining unit-cell dimensions. ω scan, scan width: $1\cdot 10^\circ$, scan speed: $0\cdot 02^\circ \text{ s}^{-1}$, total background measuring time: 6 s. 3223 reflections collected ($3 < \theta < 30^\circ$), $\pm h$, k , l , $h_{\text{max}} = 18$, $k_{\text{max}} = 17$, $l_{\text{max}} = 9$. Two orientation and intensity-control reflections ($\bar{6}40$ and 640) measured every 2 h without any significant variation. 1667 reflections after averaging Friedel pairs ($R_{\text{int}} = 0\cdot 022$). Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN77*; Main, Hull, Lessinger, Germain & Woolfson, 1977). H atoms located by difference Fourier synthesis. Anisotropic full-matrix refinement (on *F*), isotropic for H atoms. Unit weights. Final refinement using 1667 reflections (no rejection). Final $R = 0\cdot 035$ ($wR = 0\cdot 041$), $S = 1\cdot 278$, $\Delta/\sigma_{\text{max}} = 0\cdot 04$. Maximum peak height in the final difference Fourier map $0\cdot 280 \text{ e } \text{Å}^{-3}$. No secondary-extinction correction. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Enraf–

Table 1. Final atomic coordinates and B_{eq} for non-H atoms

Starred atoms have been refined isotropically. Estimated standard deviations are given in parentheses.

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Ca	0-17488 (6)	0-24882 (7)	0-1593 (1)	0-97 (1)
P(1)	0-15055 (8)	0-15864 (9)	0-6741 (2)	1-01 (2)
P(2)	0-82400 (9)	0-01642 (8)	0-9398 (2)	1-01 (2)
P(3)	0-95109 (8)	0-20767 (9)	0-8658 (2)	0-99 (2)
N(1)	0	0	0-354 (1)	2-6 (1)
N(2)	0	0	-0-012 (1)	3-5 (2)
O(E11)	0-8259 (3)	0-8364 (3)	0-4684 (4)	1-67 (6)
O(E12)	0-7925 (2)	0-7731 (3)	0-8109 (5)	1-47 (6)
O(L12)	0-1599 (3)	0-0363 (3)	0-7345 (4)	1-72 (6)
O(L13)	0-5271 (2)	0-3244 (3)	0-3062 (5)	1-61 (6)
O(E21)	0-1606 (3)	0-0647 (3)	0-0910 (4)	1-48 (6)
O(E22)	0-2269 (3)	0-4205 (3)	0-0618 (6)	1-80 (6)
O(L23)	0-9232 (3)	0-0935 (3)	0-9527 (6)	1-65 (6)
O(E31)	0-8564 (2)	0-2555 (3)	0-7788 (5)	1-47 (5)
O(E32)	0-0097 (3)	0-2670 (3)	0-0117 (5)	1-55 (6)
O(W1)	0-4374 (3)	0-8673 (3)	0-6504 (6)	2-60 (8)
O(W2)	0-3906 (4)	0-2859 (5)	0-6161 (7)	4-6 (1)
O(W3)	0-8551 (5)	0-5199 (6)	0-6632 (8)	6-0 (1)
H(1N1)	0-543 (7)	0-467 (7)	0-69 (1)	5 (3)*
H(2N1)	0-537 (6)	0-578 (7)	0-60 (1)	3 (2)*
H(1N2)	0-939 (6)	0-481 (7)	0-95 (1)	4 (2)*
H(2N2)	0-002 (8)	0-446 (8)	0-06 (1)	4 (2)*
H(1W1)	0-563 (7)	0-099 (7)	0-53 (1)	4 (2)*
H(2W1)	0-530 (7)	0-188 (7)	0-65 (1)	4 (2)*
H(1W2)	0-156 (7)	0-773 (7)	0-30 (1)	4 (2)*
H(2W2)	0-872 (7)	0-226 (7)	0-52 (1)	4 (2)*
H(1W3)	0-627 (7)	0-062 (7)	0-40 (1)	5 (3)*
H(2W3)	0-311 (8)	0-934 (7)	0-24 (1)	5 (3)*

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) in the atomic arrangement of $\text{Ca}_2(\text{NH}_4)_2\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$

Estimated standard deviations are given in parentheses.

The P_6O_{18} ring anionThe P(1) O_4 tetrahedron

P(1)	O(E11)	O(E12)	O(L12)	O(L13)
O(E11)	1-478 (3)	2-571 (5)	2-466 (4)	2-467 (5)
O(E12)	120-7 (2)	1-480 (3)	2-523 (5)	2-538 (4)
O(L12)	106-6 (2)	110-2 (2)	1-596 (3)	2-496 (5)
O(L13)	106-3 (2)	110-7 (2)	100-3 (2)	1-603 (3)

The P(2) O_4 tetrahedron

P(2)	O(L12)	O(E21)	O(E22)	O(L23)
O(L12)	1-600 (3)	2-531 (4)	2-502 (5)	2-477 (5)
O(E21)	110-2 (2)	1-484 (3)	2-550 (5)	2-457 (5)
O(E22)	108-9 (2)	119-0 (2)	1-474 (3)	2-524 (5)
O(L23)	101-4 (2)	105-5 (2)	110-3 (2)	1-600 (3)

The P(3) O_4 tetrahedron

P(3)	O(L13)	O(L23)	O(E31)	O(E32)
O(L13)	1-603 (3)	2-479 (5)	2-480 (4)	2-521 (5)
O(L23)	101-5 (2)	1-596 (4)	2-520 (5)	2-477 (5)
O(E31)	106-7 (2)	109-6 (2)	1-486 (3)	2-563 (5)
O(E32)	109-9 (2)	107-5 (2)	120-0 (2)	1-474 (3)

P(1)—P(2)	2-900 (1)	P(1)—O(L12)—P(2)	130-3 (2)
P(1)—P(3)	2-955 (1)	P(1)—O(L13)—P(3)	134-3 (2)
P(2)—P(3)	2-945 (2)	P(2)—O(L23)—P(3)	134-3 (2)
P(2)—P(1)—P(3)	87-77 (4)		
P(1)—P(2)—P(3)	116-10 (5)		
P(1)—P(3)—P(2)	112-95 (5)		

The CaO_7 polyhedron

Ca—O(E11)	2-421 (3)	Ca—O(E31)	2-368 (3)
Ca—O(E12)	2-500 (3)	Ca—O(E32)	2-369 (3)
Ca—O(E21)	2-365 (3)	Ca—O(W1)	2-464 (4)
	Ca—O(E22)	2-356 (3)	

The N(1) O_{12} polyhedron

N(1)—O(E11)	3-137 (4)	($\times 2$)	N(1)—O(E21)	2-881 (6)	($\times 2$)
N(1)—O(L12)	3-403 (7)	($\times 2$)	N(1)—O(L23)	3-207 (7)	($\times 2$)
N(1)—O(L13)	3-269 (6)	($\times 2$)	N(1)—O(W2)	3-036 (6)	($\times 2$)

The N(2) O_8 polyhedron

N(2)—O(E22)	3-095 (3)	($\times 2$)	N(2)—O(W1)	3-008 (8)	($\times 2$)
N(2)—O(E32)	2-923 (3)	($\times 2$)	N(2)—O(W3)	3-085 (9)	($\times 2$)

The hydrogen bonds

O(N)—H...O	O(N)—H	H...O	O(N)—O	O(N)—H...O
N(1)—H(1N1)...O(E21)	0-74 (9)	2-21 (9)	2-881 (6)	151 (9)
N(1)—H(2N1)...O(W2)	1-14 (8)	1-94 (8)	3-036 (6)	160 (7)
N(2)—H(1N2)...O(W3)	0-94 (8)	2-31 (9)	3-085 (9)	139 (7)
N(2)—H(2N2)...O(E32)	0-75 (8)	2-27 (8)	2-923 (3)	146 (8)
N(2)—O(W1)		2-40 (9)	3-008 (9)	138 (8)
O(W1)—H(1W1)...O(W3)	0-92 (9)	2-00 (9)	2-823 (7)	148 (7)
O(W1)—H(2W1)...O(W2)	0-81 (9)	2-18 (9)	2-935 (7)	155 (9)
O(W2)—H(1W2)...O(E12)	0-88 (9)	1-98 (9)	2-816 (6)	157 (8)
O(W2)—H(2W2)...O(E31)	1-01 (10)	1-85 (10)	2-857 (6)	172 (7)
O(W3)—H(1W3)...O(W1)	0-75 (10)	2-11 (10)	2-823 (7)	160 (10)
O(W3)—H(2W3)...O(E22)	1-07 (9)	2-17 (10)	3-084 (7)	142 (7)

H(1W1)—O(W1)—H(2W1)	112 (9)	H(1W2)—O(W2)—H(2W2)	119 (8)
H(1W3)—O(W3)—H(2W3)	101 (9)		

Nonius (1977) SDP used for all calculations. Computer used: MicroVAX II.

Discussion. Table 1 gives the final atomic coordinates.* The P_6O_{18} ring anion is located about the twofold axis parallel to the *c* axis. Table 2 gives the main geometrical features of the anion. The existence of P_6O_{18} groups with $\bar{1}$, $\bar{3}$, 3 and *m* internal symmetry has already been observed. The title compound is the first example of twofold internal symmetry in a condensed anion of this type. In spite of this internal symmetry the ring is far from regular. The P—P—P angles vary between 87.77 and 116.10°. The P(2)—P(1)—P(3) angle observed here (87.77°) is the smallest reported for a P_6O_{18} group.

The two ammonium groups are also located on the twofold axes. The first, N(1), is coordinated to ten O atoms and two water molecules. The second, N(2), has only eight neighbours: four water molecules and four O atoms. It is worth noting that six of the bonding O atoms, O(L), of the condensed phosphoric anion, make up part of the N(1) coordination polyhedron, which is rare in condensed phosphate crystal chemistry.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53085 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The Ca atom is coordinated to six O atoms and one water molecule, which lie within 2.50 Å.

The P_6O_{18} ring anions and the N(1) O_{12} polyhedra alternate along the twofold axis which is parallel to the *c* direction. They are separated by a distance of

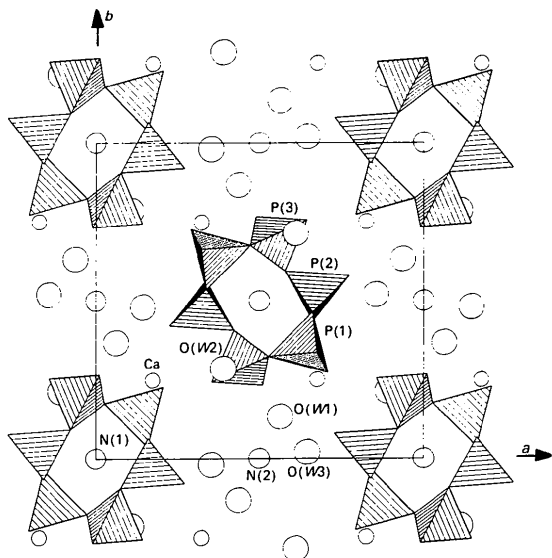


Fig. 1. Projection along the c axis showing the atomic arrangement of $\text{Ca}_2(\text{NH}_4)_2\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$. The H atoms have been omitted for clarity.

$c/2$. These rows are interconnected by the second ammonium polyhedron, the CaO_7 polyhedra and the hydrogen bonds to form a three-dimensional network whose main geometrical features are reported in Table 2.

The program *STRUPLO* (Fischer, 1985) was used to prepare Fig. 1.

References

- AVERBUCH-POUCHOT, M. T. (1989). *Acta Cryst.* **C45**, 1856–1858.
 AVERBUCH-POUCHOT, M. T. (1990). *Acta Cryst.* **C46**, 10–13.
 AVERBUCH-POUCHOT, M. T. & DURIF, A. (1990a). *Acta Cryst.* **C46**, 968–970.
 AVERBUCH-POUCHOT, M. T. & DURIF, A. (1990b). *Acta Cryst.* Submitted.
 Enraf–Nonius (1977). *Structure Determination Package*, version RSX11M. Enraf–Nonius, Delft, The Netherlands.
 FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Acta Cryst. (1990). **C46**, 2007–2009

$(\text{NH}_4)\text{Mo}_3\text{O}_9$, an Ammonium Molybdenum Bronze

BY KLAUS-JÜRGEN RANGE,* KARL BAUER AND ULRICH KLEMENT

Institute of Inorganic Chemistry, University of Regensburg, Universitätsstrasse 31, D-8400 Regensburg, Federal Republic of Germany

(Received 27 October 1989; accepted 16 February 1990)

Abstract. Ammonium trimolybdate(V,2VI), $M_r = 449.85$, monoclinic, $C2/m$, $a = 14.819(4)$, $b = 7.708(1)$, $c = 6.386(2)$ Å, $\beta = 93.56(3)^\circ$, $V = 728.0$ Å³, $Z = 4$, $D_x = 4.10$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 5.0$ mm⁻¹, $F(000) = 836$, $T = 296$ K. The structure was refined to $R = 0.074$ for 882 absorption-corrected reflections. The bronze, prepared by hydrothermal decomposition of ammonium heptamolybdate, contains units of six edge-shared MoO_6 octahedra [$\text{Mo}(1)\text{—O} = 1.67\text{--}2.29$, $\text{Mo}(2)\text{—O} = 1.68\text{--}2.38$ Å] which share vertices along $[010]$ and $[001]$ to form infinite layers. The ammonium ions completely occupy positions with an irregular eight-fold coordination ($\text{N—O} = 2.74\text{--}3.14$ Å) between the layers.

Introduction. NH_3 is a mild reducing agent for transition metal–oxygen compounds. This has been

demonstrated in a detailed study of the closed-system thermal decomposition of NH_4VO_3 (Range & Zintl, 1983; Range, Zintl & Heyns, 1988) and $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ (Range, Eglmeier, Heyns & De Waal, 1990). Redox reactions can also occur in the system $\text{NH}_3\text{—MoO}_3\text{—H}_2\text{O}$. The present paper describes the hydrothermal synthesis and structure refinement of a new ammonium molybdenum bronze, $(\text{NH}_4)\text{Mo}_3\text{O}_9$.

Experimental. $(\text{NH}_4)\text{Mo}_3\text{O}_9$ was prepared by hydrothermal decomposition of ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 2\text{H}_2\text{O}$ (silver ampoule, 500 bar, 625 K, 72 h, heating rate 5 K min⁻¹, cooling rate 0.5 K min⁻¹). The reaction product consisted of a mixture of black needles (MoO_3 , main product) and bronze-coloured crystals with nearly rectangular shape. Chemical analysis of selected bronze-coloured crystals (NH_4 found: 3.98, 4.12%; calculated: 4.01%) and EDX (only Mo, no Ag found) pointed to the stoichiometry $(\text{NH}_4)\text{Mo}_3\text{O}_9$.

* To whom correspondence should be addressed.