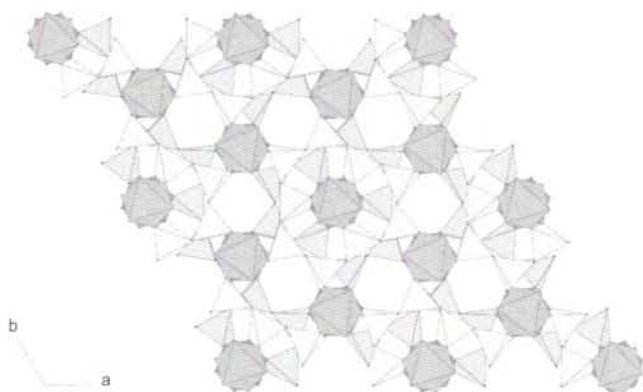


Crystal structure of aluminium cyclononaphosphate, $\text{Al}_3\text{P}_9\text{O}_{27}$

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Abstract

$\text{Al}_3\text{O}_{27}\text{P}_9$, trigonal, $P3c1$ (No. 165), $a = 10.935(2)$ Å, $c = 9.191(2)$ Å, $V = 951.8$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.037$, $wR_{\text{ref}}(F^2) = 0.094$, $T = 293$ K.

Source of material

2g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 g hot (420 K) $\text{H}_4\text{P}_2\text{O}_7$ in a gold crucible and the mixture is stored for 14 days at 520 K. Then the mixture was dissolved in water and filtered. The residue contains clear white crystals of $\text{Al}_3\text{P}_9\text{O}_{27}$ and a fine second unknown compound.

Discussion

Cyclophosphates $[\text{P}_n\text{O}_{3n}]^{n-}$ are a common class of compounds. The ring anions are known to exist for $n = 3, 4, 5, 6, 8, 9, 10$ and 12. For all cyclophosphate anions exist reliable structural data with one exception, the cyclononaphosphate anion [1]. The first suc-

cessful attempts to prepare cyclononaphosphates were made by Bagieu [2]. In this work the authors characterized $\text{Al}_3\text{P}_9\text{O}_{27}$, $\text{Fe}_3\text{P}_9\text{O}_{27}$ and a $\text{Cr}_3\text{P}_9\text{O}_{27}$ and estimated the unit cell dimensions. At this state of work they couldn't recognize the chemical nature of the compounds. Later the authors prepared an isotopic $(\text{Fe}, \text{V})_3\text{P}_9\text{O}_{27}$ and made a crystallographic investigation. Because of the inaccuracy of the investigation they didn't report any numerical values. We prepared crystals of $\text{Al}_3\text{P}_9\text{O}_{27}$ by investigations of the system $\text{H}_4\text{P}_2\text{O}_7/\text{Al}^{3+}$ and estimated the crystal structure of this compound. The structure of $\text{Al}_3\text{P}_9\text{O}_{27}$ consist of tubes with stacked P_9O_{27} -rings. The Al(1)-atom connects the rings in the tube each other. The tubes are arranged in a hexagonal symmetry and connected via the Al(2)-atom. A remarkable characteristic of the structure is, that all aluminium atoms and all phosphate rings form separate layers parallel to the $[110]$ plane. The bond distances are all in a normal range. Al(1) is surrounded by six O(1) with a Al—O distance of 1.874 Å and Al(2) is surrounded by O(2) and O(3) with distances of 1.888 Å and 1.875 Å. Phosphorus forms the typical tetrahedron with two long P—O bonds (1.57 Å) and two short P—O bonds (1.48 Å).

Table 1. Data collection and handling.

Crystal:	white prism, size $0.15 \times 0.15 \times 0.2$ mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	6.46 cm^{-1}
Diffractionmeter, scan mode:	Nonius Turbo CAD4, $\theta/2\theta$
$2\theta_{\text{max}}$:	63.92°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	5474, 935
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 725
$N(\text{param})_{\text{refined}}$:	62
Programs:	DIAMOND [3], SHELXS-90 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	6f	0.2052(1)	0	1/4	0.0063(3)	0.0060(4)	0.0090(5)	$U_{22}/2$	0.0004(2)	$2U_{13}$
Al(1)	2b	0	0	0	0.0083(6)	U_{11}	0.006(1)	$U_{11}/2$	0	0
Al(2)	4d	2/3	1/3	−0.0021(2)	0.0109(4)	U_{11}	0.0086(7)	$U_{11}/2$	0	0
P(2)	12g	0.44583(8)	0.28727(8)	0.24318(8)	0.0060(3)	0.0058(3)	0.0084(3)	0.0032(3)	0.0000(3)	0.0001(3)
O(1)	12g	0.1175(2)	−0.0383(2)	0.1165(3)	0.014(1)	0.014(1)	0.012(1)	0.0084(9)	−0.0041(8)	0.0001(8)
O(2)	12g	0.5359(2)	0.3541(2)	0.1143(3)	0.016(1)	0.012(1)	0.017(1)	0.0064(9)	0.0093(9)	0.0049(9)
O(3)	12g	0.6831(3)	0.4839(3)	−0.1145(3)	0.026(1)	0.020(1)	0.014(1)	0.013(1)	0.005(1)	0.0094(9)
O(4)	12g	0.3590(2)	0.1227(2)	0.2150(3)	0.009(1)	0.0047(9)	0.023(1)	0.0025(8)	0.0060(8)	−0.0003(8)
O(5)	6f	0.3239(3)	x	1/4	0.008(1)	U_{11}	0.022(2)	0.006(1)	−0.0002(6)	− U_{13}

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