

Table 1. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Sb(1)	0.75	0.75	0.8461 (1)	206
Cl(1)	0.0719 (2)	0.7059 (2)	0.3288 (3)	361
P(1)	0.25	0.75	0.5	241
F(1)	0.0523 (6)	0.6698 (7)	0.8461 (8)	485
F(2)	0.75	0.75	0.552 (1)	566
F(3)	0.75	0.75	1.139 (1)	458

Table 2. Bond distances (\AA) and bond angles ($^\circ$)

Anion		Cation	
Sb(1)—F(1)	1.864 (5) × 4	P(1)—Cl(1)	1.929 (2) × 4
Sb(1)—F(2)	1.924 (9) × 1	Cl—P—Cl	109.15 (8) × 2
Sb(1)—F(3)	1.912 (8) × 1	Cl—P—Cl	109.63 (8) × 4
F—Sb—F	90.0 or 180.0		

PCl₄⁺·(Sb,Nb,Ta)Cl₆⁻·AsCl₃ (Preiss & Reich, 1971); PCl₄⁺·ICl₄⁻ (Shamir, Schneider, Bino & Cohen, 1986); PCl₄⁺·PCl₆⁻ (Clark, Powell & Wells, 1942). The investigated crystal of the title compound is isomorphous with the crystals of the compounds AsCl₄⁺·AsF₆⁻ (Preiss, 1971a; Minkwitz, Nowicki & Borrmann, 1991) and PCl₄⁺·PCl₆⁻ (Preiss, 1971b).

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Structure of Aluminium Disodium Trihydrogenbis(diphosphate)

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Abstract. Na₂AlH₃(P₂O₇)₂, $M_r = 423.9$, triclinic, $P\bar{1}$, $a = 8.311$ (4), $b = 7.363$ (4), $c = 4.902$ (3) \AA , $\alpha =$

99.67 (2), $\beta = 81.77$ (2), $\gamma = 114.48$ (1) $^\circ$, $V = 268.2$ (4) \AA^3 , $Z = 1$, $D_x = 2.624$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ \AA , $\mu = 9.31$ cm⁻¹, $F(000) = 210$, $T = 293$ K, $R = 0.032$ for 761 independent observed reflections. The Al octahedron shares two opposite edges with

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two diphosphate anions. In each anion, one PO_4 tetrahedron connects two Al octahedra, forming an $\text{Al}-(\text{P}_1, \text{P}_1)-\text{Al}$ chain parallel to the c axis. The H atoms are thought to lie around the inversion centres at $(\frac{1}{2}, 0)$, $(\frac{1}{2}, 0)$ and $(0, \frac{1}{2})$ where small residual difference peaks were found. Na ions are located in tunnel-shaped cavities parallel to c .

Experimental. Crystals of the title compound were grown by the hydrothermal technique using Morey-type autoclaves at 530 K and 10 MPa. The starting materials (Na_2O , Al_2O_3 , P_2O_5 and H_2O in molar ratio 4:1:17.5:4) were placed in a teflon liner. After 7 d crystals of 0.1 to 1 mm in size were obtained. They were colourless, with a pseudo-rhombohedral shape and vitreous lustre. Details of the synthesis will be published elsewhere. The preliminary impedance spectroscopic studies carried out on these crystals show high ionic conductivity of the order of $4.1 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$ and activation energy of 0.3 eV at 1 KHz internal frequency and 573 K. A detailed study of the conduction mechanism with reference to the location of Na and H ions in the structure is under progress.

A pseudo-rhombohedral shaped edge-rounded isometric crystal with dimension 0.15 mm was used for data collection on a Philips 1100 diffractometer, with graphite monochromator. Cell dimensions were determined from setting angles of 17 reflections with $4 < \theta < 10^\circ$. Intensities were collected from $\omega/2\theta$ scans (scan rate 0.03°s^{-1} , width 1.2° in ω). 783 unique intensities with $2 < \theta < 25^\circ$ were collected, of which 22 were considered unobserved under the condition $I < 2.5\sigma(I)$. No absorption correction was applied. $-9 \leq h \leq 9$, $-8 \leq k \leq 8$, $0 \leq l \leq 5$. Three standard reflections ($\bar{1}\bar{1}3$, $2\bar{2}1$ and $\bar{2}21$) monitored every 2 h showed no variation. The structure was solved by direct methods using the *MULTAN*80 system of programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). E maps generated with 284 independent structure factors revealed fragments of diphosphate anions. With these, most of the remaining atoms were found by tangent-formula refinement of the difference structure factors (Beurskens, Bosman, Doesburg, Gould, van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981). Some O atoms were finally found by difference Fourier synthesis. Refinements were carried out by the program *SHELX76* (Sheldrick, 1976). Scattering factors for neutral atoms and f' , f'' values were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). Difference syntheses did not reveal H-atom positions with clarity. Anisotropic displacement parameters were adjusted for all other atoms. Final $R = 0.032$ ($wR = 0.036$). The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = [\sigma^2(F_o) + 0.000855F_o^2]/0.9728$. Maximum $\Delta/\sigma =$

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses

$B_{\text{eq}} = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$ for the orthogonalized U_{ij} tensor.

	x	y	z	B_{eq}
Al	0.0	0.0	0.0	0.63 (6)
P(1)	0.2617 (1)	0.0801 (1)	0.4524 (2)	0.72 (4)
P(2)	0.2300 (1)	0.4259 (1)	0.2839 (2)	0.82 (4)
O(1)	0.2114 (3)	0.0409 (4)	-0.2513 (5)	0.9 (1)
O(2)	0.0810 (3)	0.2728 (4)	0.1229 (5)	1.0 (1)
O(3)	0.1182 (3)	-0.0443 (4)	0.2598 (5)	0.9 (1)
O(4)	0.3090 (3)	0.3123 (4)	0.4389 (6)	1.2 (1)
O(5)	0.4325 (3)	0.0503 (4)	0.3419 (5)	1.2 (1)
O(6)	0.3834 (4)	0.5614 (4)	0.1068 (6)	1.6 (1)
O(7)	0.1637 (4)	0.5558 (4)	-0.5045 (6)	1.7 (1)
Na	0.2850 (2)	0.7788 (3)	-0.0913 (3)	1.81 (8)

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses

Al octahedron				
Al—O(1)	1.940 (3)	O(1)—O(2)	2.715 (3)	
Al—O(2)	1.855 (2)	O(1)—O(3)	2.616 (4)	
Al—O(3)	1.859 (2)	O(2)—O(3)	2.680 (3)	
O(1)—O(2)	2.653 (3)	O(1)—Al—O(2)	91.3 (1)	
O(1)—O(3)	2.756 (4)	O(1)—Al—O(3)	87.0 (1)	
O(2)—O(3)	2.571 (3)	O(2)—Al—O(3)	92.4 (1)	
P_2O_7 anion				
P(1)	O(1 ⁱⁱ)	O(3)	O(4)	O(5)
O(1 ⁱⁱ)	1.495 (3)	114.1 (2)	108.2 (2)	111.2 (1)
O(3)	2.522 (4)	1.510 (3)	108.3 (1)	109.3 (1)
O(4)	2.506 (4)	2.521 (4)	1.599 (3)	105.2 (1)
O(5)	2.500 (3)	2.484 (3)	2.489 (3)	1.534 (3)
P(2)	O(2)	O(4)	O(6)	O(7)
O(2)	1.500 (3)	108.8 (1)	114.2 (2)	110.9 (1)
O(4)	2.512 (3)	1.587 (3)	106.4 (1)	107.4 (2)
O(6)	2.532 (4)	2.484 (4)	1.515 (3)	108.8 (2)
O(7)	2.487 (4)	2.503 (4)	2.466 (4)	1.519 (3)
P(1)—P(2)	2.926 (1)	P(1)—O(4)—P(2)	133.3 (2)	
Na polyhedron (distances shorter than 3.000 \AA)				
Na	O(1 ⁱⁱⁱ)	O(5 ^v)	2.419 (3)	
O(1 ⁱⁱⁱ)	2.517 (3)	O(6)	2.452 (3)	
O(2 ⁱⁱⁱ)	2.929 (3)	O(7 ^{vii})	2.397 (3)	
O(3 ⁱⁱⁱ)	2.577 (3)	Mean	2.570	
O(5 ⁱⁱⁱ)	2.701 (3)			
Hydrogen-bond distances				
O(5)—H(1)—O(5 ⁱⁱⁱ)	2.405 (5)			
O(6)—H(2)—O(6 ⁱⁱⁱ)	2.494 (5)			
O(7)—H(3)—O(7 ^{vii})	2.500 (5)			

Symmetry code: (i) $-x, -y, -z$; (ii) $x, y, z + 1$; (iii) $x, y + 1, z$; (iv) $-x, -y + 1, -z$; (v) $-x, -y + 1, -z + 1$; (vi) $x, y, z - 1$; (vii) $-x + 1, -y, -z + 1$; (viii) $-x + 1, -y + 1, -z$.

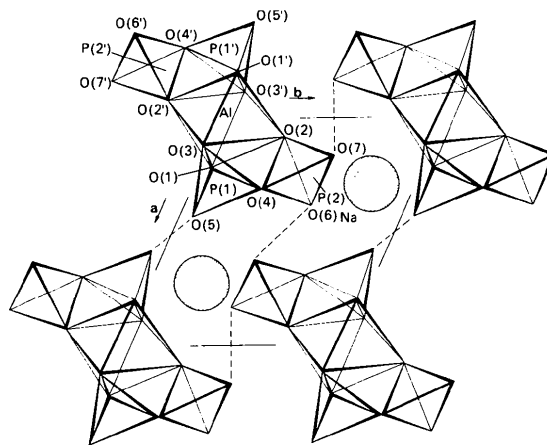


Fig. 1. Projection of the structure of $\text{Na}_2\text{AlH}_3(\text{P}_2\text{O}_7)_2$ along the c axis. Broken lines indicate hydrogen bonds.

0.01. Maximum and minimum peak heights in the final difference Fourier synthesis were 0.48 and -0.46 e \AA^{-3} . Final atomic coordinates and B_{eq} values are reported in Table 1.*

Related literature. Unindexed powder diffraction data for $\text{Na}_2\text{AlH}_3(\text{P}_2\text{O}_7)_2$ were reported previously by two independent groups (Pintard-Scrépel, Dorémieux-Morin & d'Yvoire, 1981; Grunze & Grunze, 1984). The results of the first group are in accord with those reported here whereas Grunze & Grunze described polymorphs of a compound they believed to be $\text{NaAlH}_4(\text{P}_2\text{O}_7)_2$. However, the lattice spacings for one of these match fairly well those of our compound. Doubt remains whether the second structure found by Grunze & Grunze is a polymorphic phase of $\text{NaAlH}_3(\text{P}_2\text{O}_7)_2$; it may correspond to a different compound with the composition attributed to it by these authors.

The atomic arrangement of $\text{Na}_2\text{AlH}_3(\text{P}_2\text{O}_7)_2$ projected along the c axis is shown in Fig. 1. Distorted O_6 octahedra about Al share two opposite edges [O(2)—O(3)] with two diphosphate anions. These octahedra are connected by two symmetry related P(1) tetrahedra, forming a chain parallel to [001].

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55081 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0258]

The chains are held together by the three hydrogen bonds in directions [100], [010] and [110].

Table 2 reports the main interatomic distances and bond angles. The diphosphate anion shows the expected features: the average P—O bond length is 1.532 \AA and the P(1)—O(4)—P(2) angle is 133.3° . The Na^+ ions lie in tunnel cavities parallel to [001], with seven O-atom neighbours at distances shorter than 3 \AA . The mean Na—O distance [2.570 \AA] is very similar to the values encountered in other ionic Na conductors.

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Structural Investigations of Nickel(II) Complexes. X. Tris(3,5-dimethylpiperidine)-bis(isothiocyanato)nickel(II), $[\text{Ni}(\text{NCS})_2(3,5\text{-diMepip})_3]$

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Abstract. $[\text{Ni}(\text{NCS})_2(\text{C}_7\text{H}_{15}\text{N})_3]$, $M_r = 514.5$, triclinic, $P\bar{1}$, $a = 10.41$ (1), $b = 10.63$ (2), $c = 13.63$ (2) Å , $\alpha = 81.8$ (1), $\beta = 76.6$ (1), $\gamma = 69.8$ (1) $^\circ$, $V = 1373.7$ (4.1) Å^3 , $Z = 2$, $D_m = 1.19$, $D_x = 1.24 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71070 \text{ Å}$, $\mu = 8.7 \text{ cm}^{-1}$, $F(000) = 556$, room temperature, $R = 0.0568$, $wR = 0.0567$ for 975 reflections with $I \geq 3\sigma(I)$. The crystal is formed by monomeric units of $[\text{Ni}(\text{NCS})_2(3,5\text{-diMepip})_3]$. The two N atoms of two NCS groups and three 3,5-diMepip ligands define a tetragonal pyramid about the Ni atom. The axial site contains a 3,5-diMepip

ligand and the basal plane pairs of *trans* NCS $^-$ and 3,5-diMepip ligands.

Experimental. Green prism-shaped crystals of poor quality, $0.51 \times 0.31 \times 0.23 \text{ mm}$; density measured by flotation. A Syntex $P2_1$ four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation was used for data collection. 15 reflections with $4.91 \leq \theta \leq 12.72^\circ$ were used for determination of the lattice parameters. Absorption and extinction were ignored. Intensity measurements from θ – 2θ scans were made