

2,966 Å. Chacun d'eux relie entre eux deux tétraèdres  $P(1)O_4$  et un tétraèdre  $P(2)O_4$ .

Les distances P—O ont ici en moyenne pour valeur: 1,537 Å dans le tétraèdre  $P(1)O_4$  et 1,534 Å dans le tétraèdre  $P(2)O_4$ . Les distances zinc—phosphore rapportées dans le Tableau 2, toutes inférieures à 3,25 Å, sont plus courtes que celles généralement observées dans les autres phosphates de zinc (Zn—P ~ 3,5 Å).

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## Sodium Tetrahydroaluminate\*

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**Abstract.**  $NaAlH_4$ , tetragonal,  $I4_1/a$ ,  $a = 5.020$  (2),  $c = 11.330$  (3) Å, (Mo  $K\alpha$ ,  $T = 296$  K),  $V = 285.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.256$  Mg m<sup>-3</sup>,  $R = 0.039$ ,  $R_w = 0.062$ . Each metal atom sits at a site of  $\bar{4}$  ( $D_{2d}$ ) symmetry. The  $AlH_4^-$  anion has a compressed tetrahedral geometry with Al—H distances of 1.532 (7) Å and unique angles of 113.9 (5) and 107.3 (3)°. The Na atom has eight nearest-neighbor H atoms which define the vertices of a distorted triangular dodecahedron.

**Introduction.** At present a study is underway to investigate the chemical reactivity of solid aluminum hydride (Herley & Irwin, 1978) and the alkali-metal tetrahydroaluminates (Herley & Schaeffer, 1978; Herley & Spencer, 1979). The reactivities of the solids depend markedly upon the solid-state defects present in the crystallographic habit surfaces. Thus a detailed knowledge of the crystal topography is necessary to understand the mechanisms of the decomposition processes. The detailed crystal structures of  $AlH_3$  (Turley & Rinn, 1969) and  $LiAlH_4$  (Sklar & Post, 1967) are known. The unit cell of  $NaAlH_4$  is known to be tetragonal (Subrtova, 1967; Bakulina, Bakum & Dymova, 1968), but to date a complete structure has not been reported. We report here a complete structure analysis for  $NaAlH_4$  single crystals.

Single crystals of  $NaAlH_4$  were prepared using the following procedure. (All manipulations were carried out in a nitrogen-filled glove box and in sealed nitrogen-

flushed glassware which was baked for 12 h at 413 K prior to use.) Impure  $NaAlH_4$  was obtained from Alfa Division, Ventron Corporation, Danvers, Massachusetts. The tetrahydrofuran solvent (Fisher certified reagent) was distilled over  $NaAlH_4$  just prior to use. The  $NaAlH_4$  powder was introduced into the solvent at room temperature, stirred overnight, then centrifuged (4000 r.p.m. for 20 min) in sealed tubes. The clear supernatant solution was transferred to a Pyrex-glass crystallizer through which PPG nitrogen was passed at ~323 K to assist evaporation. The aggregated single crystals were transparent, cubic in shape, approximately 1 mm on a side, and tinged gray.

The crystal selected for data collection was a fragment of approximate dimensions 0.6 × 0.3 × 0.15 mm. The crystal was sealed in a glass capillary and mounted on an Enraf-Nonius CAD-4A diffractometer under the control of a PDP 1145 computing system. The cell dimensions were determined by a least-squares analysis of the settings of 25 reflections (Mo  $K\alpha$  radiation at 296 K) and are in good agreement with those reported earlier by Subrtova (1967) and Bakulina, Bakum & Dymova (1968). Data were collected using Mo  $K\alpha$  radiation with a graphite monochromator. The  $\omega$ - $2\theta$  scanning mode was used with  $\theta < 60^\circ$ . The data were processed using the Enraf-Nonius structure determination package developed by Okaya (1978) and Frenz (1978). Of the 2985 data measured, 667 reflections were unique and measured with  $I > 3.0\sigma(I)$ . The structure was solved by Patterson methods which clearly defined positions for the three unique atoms. The structure was refined using

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Table 1. *Positional and thermal parameters and their estimated standard deviations*

The form of the anisotropic thermal parameter is:  $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

	x	y	z	$\beta_{11}, \beta_{22}$	$\beta_{33}$	$\beta_{12}, \beta_{13}, \beta_{23}$
Al	0	0	0	0.0139 (1)	0.00362 (2)	0
Na	0	0	$\frac{1}{2}$	0.0255 (3)	0.00446 (4)	0
H	0.228 (1)	0.117 (2)	0.838 (9)	$B = 1.8 (2) \text{ \AA}^2$		

a full-matrix least-squares method with the Na and Al atoms assigned anisotropic temperature factors and the H atom assigned an isotropic temperature factor. There was no evidence for extinction and no absorption correction was applied since the coefficient ( $\mu = 0.498 \text{ mm}^{-1}$ ) was small. The final values of  $R$  and  $R_w$  were 0.039 and 0.062 for the 667 reflections and 9 variables used in the refinement procedure.  $R$  and  $R_w$  are defined as:  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$ ;  $w = 1/(\sigma^2 + 0.016F^2)$ ; the function minimized was  $\sum w(|F_o| - |F_c|)^2$ . The error in an observation of unit weight was 1.75 electrons. Final atomic parameters are given in Table 1.\*

**Discussion.** The crystal packing of  $\text{NaAlH}_4$  is shown in Fig. 1. Each metal atom sits at a site of 4 ( $D_{2d}$ ) symmetry. The coordination polyhedron of the Al atom (Fig. 2) is a distorted tetrahedron with Al—H bond distances of 1.532 (7) Å. The tetrahedron is compressed along the 4 axis with unique bond angles of

113.9 (5) and 107.3 (3)°. The Na atom has eight H atoms as nearest neighbors, which define the vertices of a distorted triangular dodecahedron (Fig. 3). The two unique Na—H bond distances are essentially identical, 2.504 (7) and 2.490 (7) Å. Each H atom is bound to one Al atom and is 2.504 (7) Å from one Na atom and 2.490 (7) Å from a second Na atom.

The Al—H bond distance [1.532 (7) Å] found for the  $\text{AlH}_4^-$  anion is in good agreement with the 1.55 (2) Å reported for the anion of  $\text{LiAlH}_4$  (Sklar & Post, 1967) and represents a normal Al—H covalent bond. In  $\text{AlH}_3$  (Turley & Rinn, 1969) each H atom bridges two Al atoms forming a three-center two-electron bond. Each Al atom is thus six coordinate with an Al—H bond distance of 1.72 Å. It should be noted that all of the H distances quoted here suffer an expected systematic error due to the asphericity of the electron distribution around the H atom. Neutron diffraction data would be required to accurately locate the H nuclei.

The geometry of the Na ions is most unusual, with the eight nearest-neighbor H atoms defining a nearly regular triangular dodecahedron. In  $\text{LiAlH}_4$  the smaller

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34321 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

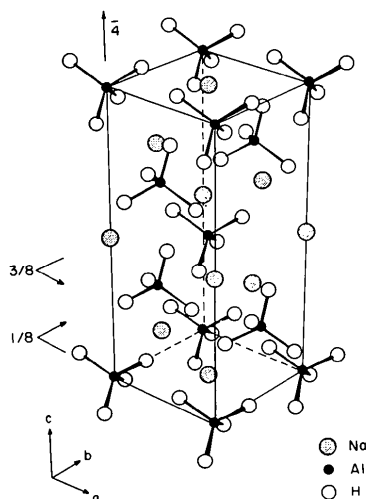


Fig. 1. The unit cell of  $\text{NaAlH}_4$ . Each metal atom sits at a site of  $\bar{4}$  ( $D_{2d}$ ) symmetry.

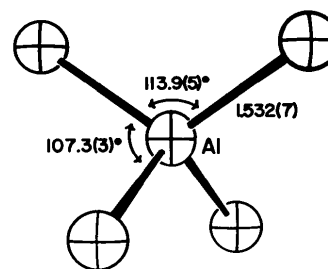


Fig. 2. The tetrahydroaluminate anion.

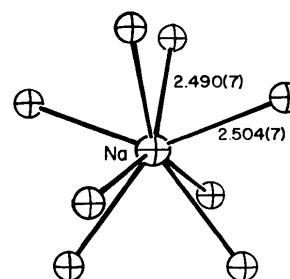


Fig. 3. The Na atom and its eight nearest-neighbor H-atom contacts. The eight H atoms define the vertices of a distorted triangular dodecahedron.

Li ions are only five coordinate with a distorted trigonal-bipyramidal coordination. Studies of the tetrahydroaluminates of the larger alkali-metal cations are underway and may prove to be equally interesting.

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## Structure du Dichromate de Cadmium–Potassium Dihydraté: $\text{CdK}_2(\text{Cr}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$

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**Abstract.**  $\text{CdK}_2(\text{Cr}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ , triclinic,  $P\bar{1}$ ,  $a = 7.999$  (3),  $b = 7.956$  (3),  $c = 6.733$  (3) Å,  $\alpha = 115.18$  (5),  $\beta = 80.55$  (5),  $\gamma = 96.11$  (5)°,  $Z = 1$ ,  $D_x = 2.86$  Mg m<sup>-3</sup>. The crystal structure has been solved by using 2662 independent reflexions, with a final  $R$  value of 0.038. The Cd atom is octahedrally coordinated to four O atoms of the  $\text{Cr}_2\text{O}_7$  groups and two water molecules. The K atoms are coordinated to seven O atoms and one water molecule.

**Introduction.** Dans une solution saturée de bichromate de potassium on ajoute une quantité d'anhydride chromique suffisante pour obtenir dans cette solution un rapport Cr/K = 3/2. La liqueur obtenue est alors portée à l'ébullition puis additionnée de carbonate de cadmium jusqu'à apparition d'un louche de couleur marron. La liqueur filtrée est ensuite abandonnée à température ambiante. Les premiers cristaux de  $\text{CdK}_2(\text{Cr}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$  apparaissent au bout de quelques jours sous la forme de prismes tricliniques trapus de couleur marron foncé. C'est un fragment de prisme de ce type, approximativement taillé en forme de cube de 0,12 mm d'arête, qui a été utilisé pour la détermination de la structure.

A l'aide de ce cristal 3036 réflexions ont été mesurées en utilisant un diffractomètre Philips PW 1100 fonctionnant à la longueur d'onde de l'argent (0,5608 Å) monochromatisée par une lame de graphite. Les mesures étaient effectuées à la vitesse de 0,02° s<sup>-1</sup> dans un domaine angulaire s'étendant de 4 à 30° ( $\theta$ ). Chaque réflexion était explorée en balayage  $\omega$  seul dans

un domaine de 1,2° aux extrémités duquel le fond continu était mesuré durant 10 s. De ces mesures, 2786 réflexions indépendantes, telles que  $I > 100$  dans notre échelle de mesure qui s'étend de 1 à 22 999, ont été conservées pour l'étude de la structure.

L'utilisation du programme *MULTAN* (Main, Woolfson & Germain, 1971) fournit les positions des atomes de chrome et de cadmium. A partir de ces données des synthèses de Fourier tridimensionnelles mettent en évidence la totalité de l'arrangement atomique. A ce stade, quelques cycles d'affinement utilisant des paramètres thermiques anisotropes (Prewitt, 1966) conduisent rapidement à une valeur finale de 0,038 de l'indice résiduel  $R$  ceci pour les 2662

Tableau 1. *Coordonnées des positions atomiques* ( $\times 10^4$ ) pour  $\text{CdK}_2(\text{Cr}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$  et  $B_{\text{eq}}$  (Å<sup>2</sup>)

Les valeurs des écarts standard sont données entre parenthèses.

	$x$	$y$	$z$	$B_{\text{eq}}$
Cd	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1,49
Cr(1)	3301,7 (7)	-102,9 (7)	2761,5 (9)	1,72
Cr(2)	1448,0 (7)	7070,9 (8)	4509,6 (9)	1,66
K	8186 (1)	7740 (1)	606 (1)	2,58
O(L)	2303 (3)	9364 (4)	5009 (4)	2,01
O(E11)	4059 (6)	2001 (5)	3743 (6)	4,25
O(E12)	4765 (4)	8417 (4)	1395 (5)	2,80
O(E13)	1904 (5)	9598 (6)	1164 (6)	3,36
O(E21)	2958 (3)	5570 (4)	3373 (5)	2,16
O(E22)	82 (4)	6524 (5)	2815 (7)	3,47
O(E23)	9367 (5)	2885 (5)	3132 (6)	3,36
O(W)	6787 (4)	4605 (5)	1843 (5)	2,50