

A New Sodium Aluminate $\text{Na}_{17}\text{Al}_5\text{O}_{16}$

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Reaction of sodium oxide with alumina has produced a new sodium aluminate $\text{Na}_{17}\text{Al}_5\text{O}_{16}$ (monoclinic, space group Cm) and an X-ray crystal structure determination has shown it to consist of discrete Al_5O_{16} chains composed of five AlO_4 tetrahedra sharing corners, with almost linear angles about the bridging oxygens.

We have previously reported¹ the structure determinations of the first two alkali-rich sodium aluminates $\text{Na}_7\text{Al}_3\text{O}_8$ and Na_5AlO_4 and this paper reports the third compound in the series. The new aluminate $\text{Na}_{17}\text{Al}_5\text{O}_{16}$ was formed from the solid-state reaction of Na_2O with $\alpha\text{-Al}_2\text{O}_3$ at 700 °C for 24 h in the molar ratio of 4:1 under a flowing argon atmosphere.

The product was in the form of a white, hygroscopic, microcrystalline solid which had to be handled and manipulated in an Ar-filled evacuable dry box to avoid atmospheric contamination. A suitable needle-like crystal was sealed into a 0.2 mm Lindemann glass capillary tube, and this was used for a full crystal structure determination.

Crystal Data: $\text{Na}_{17}\text{Al}_5\text{O}_{16}$, $M = 781.7$, monoclinic, space group Cm , $a = 5.961$, $b = 32.769$, $c = 5.989$ Å, $\beta = 120.07^\circ$, $Z = 2$, $D_c = 2.56$ g cm⁻³, $F(000) = 760$, $\mu(\text{Mo-K}\alpha_1) = 7.48$ cm⁻¹.†

X-Ray data in the range $1^\circ < \theta < 30^\circ$ were collected on a Hilger and Watts four-circle computer-controlled diffractometer. Attempts to solve the structure using direct methods were unsuccessful and so the positions of all the Al and O atoms had to be determined by interpretation of a sharpened Patterson map. This, together with packing considerations, suggested chains composed of 5 Al and 16 O atoms and gave the approximate positions of all these atoms relative to the central Al(1) which had to lie on the mirror plane. Its position was taken to define the origin of the cell in Cm . Successive structure factor calculations and Fourier syntheses, based initially on the approximate Al and O positions using the CRYSTALS program,² revealed the positions of all the sodium atoms. The positions and thermal parameters of all the atoms were then refined by least-squares methods to $R = 0.0538$, $R_w = 0.0630$ for 676 independent reflections with

intensities $I > 3\sigma(I)$. Neutral atomic scattering factors were used.³

The compound $\text{Na}_{17}\text{Al}_5\text{O}_{16}$ has a framework of AlO_4 tetrahedral units, sharing corners to form discrete zig-zag Al_5O_{16} chains running parallel to the b -axis (Figure 1). The Al–O bond distances vary between 1.70(2) and 1.80(2) Å with tetrahedral bond angles between 106(1) and 116.4(7)°. The bridging oxygens have Al–O–Al angles of 173(1) and 159.9(7)°. The co-ordination of the sodium atoms is complex. Four-fold co-ordination exists for Na(1), Na(2), Na(7), Na(8), and Na(9), the remainder being five-co-ordinate. The O–Na–O angles vary between 66.2(6) and 136.0(6)° and the Na–O bond lengths between 2.22(1) and 2.89(2) Å.

Generally, where oxygen is two-co-ordinate and has two unshared electron pairs in the valence shell, the X–O–X angle varies between 104.5° in H_2O and 111° in $(\text{CH}_3)_2\text{O}$. However, in the aluminates, the highly electronegative field created by the oxygen may lower the energies and reduce the sizes of the vacant 3d orbitals on aluminium sufficiently to allow some (d–p) π overlap.⁴ If this occurs, it is expected that the Al–O bonds would be shortened and the angle about oxygen increased. The shortening cannot be confirmed, in the absence of standards of reference, but the angles as high as 173(1)° in $\text{Na}_{17}\text{Al}_5\text{O}_{16}$ may be interpreted in terms of this type of overlap. A comprehensive analysis of the role of d-orbitals in the bonds between Si, P, S, and Cl with O or N is given by Cruickshank,⁵ involving (3d–2p) π overlap and this, together with other theories of bonding in silicates which may be relevant to aluminate structures are reviewed by Dent Glasser.⁶

The unusual formula $\text{Na}_{17}\text{Al}_5\text{O}_{16}$ nearly corresponds to the formula Na_5AlO_3 which would be the stoichiometry if the chains of tetrahedra were infinite. The fact that they are five aluminium atoms long gives rise to the stoichiometry $\text{Na}_{3.4}\text{AlO}_{3.2}$. The crystal structures of the compounds $\text{K}_6\text{Fe}_2\text{O}_6$,⁷ $\text{K}_6\text{Ga}_2\text{O}_6$,⁸ and $\text{K}_6\text{Al}_2\text{O}_6$ ⁹ have been determined and they consist of two MO_4 tetrahedra sharing an edge to form M_2O_6 dimers. The compounds Na_3FeO_3 ¹⁰ and Na_3GaO_3 ⁸ have also been reported, but no structural determinations have been

† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

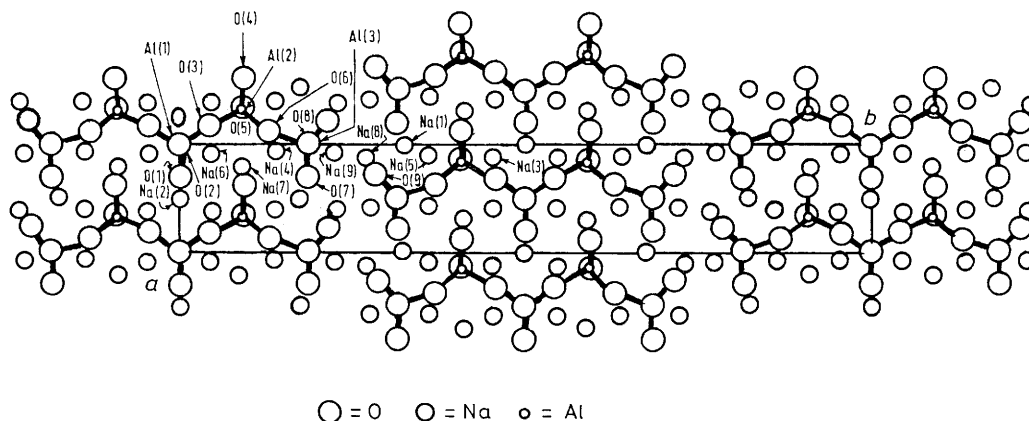


Figure 1. The crystal structure of $\text{Na}_{17}\text{Al}_5\text{O}_{16}$, viewed along the c -axis showing the co-ordination of oxygen about aluminium. Bond lengths: Al(1)–O(1) 1.75(2), Al(1)–O(2) 1.71(3), Al(1)–O(3) 1.76(2), Al(1)–O(3') 1.76(2), Al(2)–O(3) 1.77(2), Al(2)–O(4) 1.70(2), Al(2)–O(5) 1.78(1), Al(2)–O(6) 1.80(2), Al(3)–O(6) 1.78(1), Al(3)–O(7) 1.78(1), Al(3)–O(8) 1.71(2), Al(3)–O(9) 1.74(1) Å. Bond angles: O(3)–Al(1)–O(1) 111(1), O(3')–Al(1)–O(2) 106(1), O(3')–Al(1)–O(3) 106(1), O(3)–Al(1)–O(1) 111(1), O(3)–Al(1)–O(2) 106(1), O(2)–Al(1)–O(1) 114(1), O(6)–Al(2)–O(3) 107.1(9), O(6)–Al(2)–O(4) 107.2(9), O(9)–Al(3)–O(8) 108.8(8), O(9)–Al(3)–O(7) 108.8(7), O(9)–Al(3)–O(6) 109.7(8), O(8)–Al(3)–O(7) 116.5(7), O(8)–Al(3)–O(6) 106.6(8), O(7)–Al(3)–O(6) 106.4(8), O(5)–Al(2)–O(4) 111.6(7), O(4)–Al(2)–O(3) 109(1), O(5)–Al(2)–O(3) 110.9(9), Al(1)–O(3)–Al(2) 173(1), Al(2)–O(6)–Al(3) 159.9(7)°.

carried out and since their stoichiometries have not been exactly determined they may also consist of the short chains found in $\text{Na}_{3.4}\text{AlO}_{3.2}$, rather than the M_2O_6 dimers found elsewhere.

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