

## Ethylene Glycolate Derivatives of Aluminum: Tetra-, Penta-, and Hexacoordination

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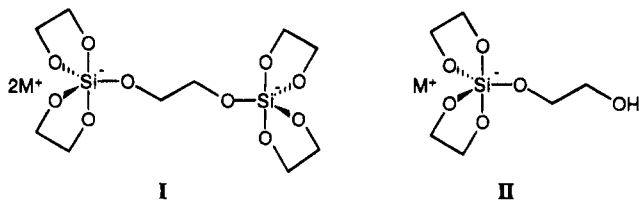
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Reactions between alumina and sodium hydroxide in ethylene glycol result in the formation of aluminoglycolate anions. <sup>27</sup>Al NMR studies have been carried out to assist in their characterization, and aluminum species in tetra-, penta-, and hexacoordinate geometries have been detected. X-ray diffraction studies of crystalline products confirm the formation of pentacoordinate dianions; two crystalline forms of a 2:1 Na:Al complex have been isolated, containing different amounts of solvent molecules. The compound Na<sub>2</sub>Al(OCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH·4HOCH<sub>2</sub>CH<sub>2</sub>OH (1) crystallizes in space group *P* $\bar{1}$ , with *a* = 8.062(2) Å, *b* = 8.660(2) Å, *c* = 17.257(3) Å;  $\alpha$  = 99.78(3)°,  $\beta$  = 97.61(3)°,  $\gamma$  = 97.08(3)°, *Z* = 2 at 130 K; Na<sub>2</sub>Al(OCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH·5HOCH<sub>2</sub>CH<sub>2</sub>OH (2) crystallizes in space group *P* $\bar{1}$ , with *a* = 8.479(3)°, *b* = 19.557(5)°, *c* = 16.641(5) Å;  $\alpha$  = 90.48(3)°,  $\beta$  = 96.68(2)°,  $\gamma$  = 89.22(2)°, and *Z* = 4 at 291 K. A third complex isolated has a 1:1 Na:Al ratio and contains a trimeric aluminum species consisting of two pentacoordinate and one hexacoordinate aluminum geometries: Na<sub>3</sub>Al<sub>3</sub>(OCH<sub>2</sub>CH<sub>2</sub>O)<sub>5</sub>(OCH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>·6HOCH<sub>2</sub>CH<sub>2</sub>OH (3) crystallizes in space group *P*2<sub>1</sub>/*c*, with *a* = 9.531(2) Å, *b* = 21.490(4) Å, *c* = 22.298(4) Å,  $\beta$  = 99.41(3)°, and *Z* = 4 at 130 K. The intermolecular binding in the three structures involves extensive hydrogen bonding between coordinated and free glycolate molecules coupled with close cation···O ionic contacts. The Al–O bond distance for the monobasic glycolates is significantly shorter than the fully coordinated bond distances (means 1.783(9), 1.846(28) Å), though ionic contacts also perturb the coordination geometries.

## Introduction

The transformation of silica into silica–sodalite using ethylene glycol as the solvent<sup>1</sup> has been convincingly demonstrated<sup>2</sup> to be *via* pentacoordinate silicon species of a type initially isolated by Laine *et al.*<sup>3,4</sup> and us,<sup>5</sup> from reactions with base in ethylene glycol. Hydrolysis and condensation of the species I or II to form the sodalite framework occurs in a sealed bomb at 150 °C under autogenous pressure.<sup>1,2</sup> Related metalloglycolates formed from alkaline glycol have been reported for titanium<sup>6</sup> and aluminum,<sup>7</sup> although the exact nature of the Al species has not been determined.



We have been studying the formation of sodalites in various glycol systems.<sup>8</sup> In the aluminosilicate sodalites, Al substitutes

for Si in the sodalite lattice and sufficient sodium ions are incorporated to maintain charge neutrality. It seems likely that an anionic aluminoglycolate species of some form is implicated in the mobile phase during the incorporation of alumina into the sodalite framework in these non-aqueous syntheses, since some glycols only form zeolites in the presence of aluminum. Ethylene glycol will react with certain reactive aluminas in the absence of base. Reaction of ethylene glycol with gibbsite<sup>9</sup> (a modification of aluminum hydroxide) has been reported to form an intercalated glycol derivative of boehmite. “Glycothermal” treatment of aluminum alkoxide results in the formation of an identical structure.<sup>10</sup> These reactions suggest that this system may not be straightforward, and the mechanism of the incorporation of aluminum into the sodalite framework may be quite complex.

Cruikshank and Dent Glasser<sup>11</sup> have determined the X-ray crystal structure of a barium aluminoglycolate formed under similar reaction conditions to the sodalite preparations, in a sealed bomb under autogenous pressure, where the liberated water was retained in the reaction mixture. Its failure to hydrolyze and recondense to form a framework aluminate shows it has a different reactivity to the aluminoglycolate species formed in the presence of sodium hydroxide. The crystal structure consists of an anionic polymer of  $\mu$ -bridged aluminoglycolate dimers linked by bridging glycolate ligands.<sup>11</sup> The aluminum atoms have pentacoordinate geometry and this compound was the subject of the first observation of pentacoordinate aluminum by <sup>27</sup>Al solid state NMR.<sup>12</sup> The polymeric

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, September 15, 1995.

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nature of the structure may explain its decreased solubility and increased stability toward hydrolysis.

We examine here the products from the reaction between sodium hydroxide, ethylene glycol, and alumina and attempt to characterize the aluminoglycolate anions produced. These species are expected to be soluble in ethylene glycol and be readily hydrolyzable as they enable the alumina to be incorporated into a sodalite framework. Parallel reactions using aluminum triisopropoxide were also carried out.  $^{27}\text{Al}$  NMR data are included and X-ray crystal structures of isolated species are reported. The complexity of this system becomes apparent as analysis of the crude, the ground crystals and single crystals give different results.

### Experimental Section

All syntheses and manipulations were carried out under an atmosphere of dry argon. Representative syntheses are described below. Solvents were dried using standard techniques and stored over molecular sieves. "Pseudo-boehmite" was prepared in our laboratory<sup>13</sup> via the hydrolysis of aluminum triisopropoxide, and had the approximate formula  $\text{AlO}(\text{OH})\cdot\text{H}_2\text{O}$ . Solution NMR spectra were run using a Bruker AC300 NMR spectrometer. The solid state CP/MAS NMR spectra were recorded on a Varian 500 MHz instrument, using an external reference,  $(1\text{ M } [\text{Al}(\text{H}_2\text{O})_6]^{3+}, \delta = 0\text{ ppm})$ . Thermogravimetric and differential thermal analyses (TGA/DTA) were obtained using a Polymer Laboratories PL-STA instrument. A ramp rate of  $10\text{ }^\circ\text{C}/\text{min}$  was commonly used, under an atmosphere of flowing oxygen-free nitrogen or dry air. X-ray diffraction (XRD) powder patterns were obtained using a Philips PW1700 series automated powder diffractometer;  $\text{Co K}\alpha$  radiation ( $1.7903\text{ \AA}$ ) was used with an automatic divergence slit and graphite diffracted beam monochromator. The samples remained under a dry atmosphere throughout preparation and data collection.

**Synthesis. Reaction of Sodium Hydroxide, Pseudo-Boehmite, and Ethylene Glycol. Method a. Using a 2:1 Na:Al Ratio.** Sodium hydroxide (1.60 g, 0.04 mol) and pseudo-boehmite (1.56 g, 0.02 mol) were stirred vigorously in ethylene glycol ( $200\text{ cm}^3$ ) as the temperature was increased. The glycol was slowly distilled off at a rate of  $ca\ 20\text{ cm}^3\text{ h}^{-1}$  so as to remove any liberated water from the reaction. After 1 h the solution was virtually clear. The distillation was continued for a total of 2 h, when the reaction mixture was cooled and filtered through Celite. The glycol was reduced to  $ca\ 50\text{ cm}^3$  by vacuum distillation. The solution was cooled, and acetonitrile ( $100\text{ cm}^3$ ) was added. The product precipitated out as a white solid. After this mixture was left for 16 h, the solid was filtered off, washed with acetonitrile ( $3 \times 20\text{ cm}^3$ ) and dried *in vacuo* at room temperature. Yield: 8.78 g.  $^{27}\text{Al}$  NMR  $\delta = 38.3\text{ ppm}$ . Slow diffusion of acetonitrile vapor into the aluminoglycolate solution over several days produced crystalline needles of **1** growing in clumps. A crystalline mixture of **1** and **2** grew over a period of several weeks. A more concentrated solution in ethylene glycol (5.0 g in  $100\text{ cm}^3$ ) with acetonitrile added ( $10\text{ cm}^3$ ) yielded approximately 3.5 g of roughly hexagonal plates of **2** over a period of a few days. The mother liquor subsequently yielded more of these crystals (not isolated) on addition of more acetonitrile.

**Method b. Using a 1:1 Na:Al Ratio.** A white crystalline product was precipitated, using sodium hydroxide (0.8 g, 0.02 mol) and pseudo-boehmite (1.56 g, 0.02 mol) reacted according to Method a. above. Yield: 4.2 g.  $^{27}\text{Al}$  NMR:  $\delta = 51.3, 9.9\text{ ppm}$ , ratio 2:1. Single crystals of **3** for X-ray analysis were grown from the mother liquors over a period of 2 weeks.

**Method c. Using a 3:1 Na:Al Ratio.** The same procedure was followed as in method a. above using sodium hydroxide (2.4 g, 0.06 mol) and pseudo-boehmite (1.56 g, 0.02 mol) to give a white crystalline mass. Yield: 6.0 g.  $^{27}\text{Al}$  NMR:  $\delta = 51.0, 41.1, 19.3\text{ ppm}$ , ratio 5:20:1.

**Table 1.** Crystallographic Data and Details of Data Collection and Structure Analyses

	1	2	3
chem formula	$\text{C}_{14}\text{H}_{37}\text{AlNa}_2\text{O}_{14}$	$\text{C}_{16}\text{H}_{43}\text{AlNa}_2\text{O}_{16}$	$\text{C}_{26}\text{H}_{66}\text{Al}_3\text{Na}_3\text{O}_{26}$
fw	502.4	564.5	944.7
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
<i>a</i> , Å	8.062(2)	8.479(3)	9.531(2)
<i>b</i> , Å	8.660(2)	19.557(5)	21.490(4)
<i>c</i> , Å	17.257(3)	16.641(5)	22.298(4)
$\alpha$ , deg	99.78(3)	90.48(3)	90
$\beta$ , deg	97.61(3)	96.68(2)	99.41(3)
$\gamma$ , deg	97.08(3)	89.22(2)	90
$N_{\text{REF}}$ , range, $^\circ$ deg	36, 11–31	30, 20–30	26, 5–27
<i>V</i> , Å <sup>3</sup>	1163.7(4)	2741(2)	4506(2)
<i>Z</i>	2	4	4
<i>T</i> , K	130(2)	293(2)	130(2)
$\rho$ , $\text{mg}\cdot\text{m}^{-3}$	1.434	1.368	1.393
$\mu(\text{Mo K}\alpha)$ , $\text{mm}^{-1}$	0.200	0.184	0.207
no. of unique data	4079	8426	5869
no. of significant data <sup>b</sup>	2952	5948	2544
no. of variables	374	691	443
<i>S</i> , goodness of fit <sup>c</sup>	1.036	1.043	1.039
index range, <i>h</i>	0 to 9	−9 to 9	0 to 10
index range, <i>k</i>	−10 to 10	−22 to 22	0 to 23
index range, <i>l</i>	−20 to 20	0 to 19	−23 to 23
$\theta$ collcn range, deg	2.4–25.0	2.1–24.0	2.1–22.5
wt params <i>P</i> <sub>1</sub> , <i>P</i> <sub>2</sub> <sup>d</sup>	0.0572, 1.33	0.0732, 22.18	0.0864, 28.46
Final mean, max shift/esd	0.005, 0.095	0.004, 0.090	0.001, 0.012
$R(F_o)^e$ , $R_w(F_o^2)^f$	0.048, 0.111	0.091, 0.234	0.101, 0.20

<sup>a</sup> Number of reflections used, range in  $2\theta$  for cell refinement. <sup>b</sup>  $F_o/I$  ( $\sigma(F_o) > 4.0$ ). <sup>c</sup>  $S = (\sum w(F_o^2 - F_c^2)^2 / (n - p))^{1/2}$ . <sup>d</sup> See text. <sup>e</sup>  $R = \sum(|F_o|_2 - |F_c|) / \sum|F_o|$ . <sup>f</sup>  $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

### Reaction of Sodium Hydroxide with Aluminium Triisopropoxide.

Sodium hydroxide (1.60 g, 0.04 mol) was stirred vigorously in ethylene glycol ( $200\text{ cm}^3$ ) and the mixture heated to remove  $20\text{ cm}^3$  of the solvent by distillation. On cooling, aluminum triisopropoxide (4.09 g, 0.02 mol) was added and the mixture stirred and reheated to  $150\text{ }^\circ\text{C}$ . After 1 h the solution was cooled, filtered, and reduced to  $ca\ 50\text{ cm}^3$  by vacuum distillation. The product precipitated on addition of dry acetonitrile ( $100\text{ cm}^3$ ). Yield: 8.6 g. An XRD trace of the crude product matched very closely with the product obtained from pseudo-boehmite in Method a. above.

**X-ray Crystallography.** Single crystals of **1** and **3** were rapidly cut to size in air and mounted on a glass fiber under a  $\text{N}_2$  cold stream on a Nicolet P3 diffractometer. Crystals of **2** were cleaved under Nujol oil, inserted into and sealed in capillaries and mounted on a Nonius CAD-4 diffractometer. Crystallographic data is collected in Table 1. Crystal **2** was collected at room temperature as the crystals appeared to crack in the cold stream; crystals **1** and **3** were collected using  $\omega$  scans, and  $\theta$ – $2\theta$  scans were used for **2** to cover the small splitting in  $2\theta$  observed. All crystals showed no degradation during data collection as monitored every 100 reflections. The data were processed and corrected for Lorentz and polarization effects.

All structures were solved by direct methods,<sup>14</sup> with successive difference fourier calculations identifying most of the hydrogen atoms, including those on the free glycol molecules when these were ordered. Disorder was present for the uncoordinated monobasic oxygen of the bound glycol in the first anion in **2** (atoms labeled O(6A) and O(6B)), for oxygens of free glycols (e.g. atoms O(29A), O(29B) in **2**; O(12A), O(12B) in **1**) and in the C–C linkage of free glycols (e.g. C(13A), C(13B) in **1**; C(18A), C(18B) in **3**). Eight of the twenty glycol molecules of crystallization in the three structures were partially disordered—these could be modelled satisfactorily as single atoms shared between two sites. In **2**, an unresolved glycol was modelled using carbon scattering at two shared sites, with one common isotropic thermal parameter (atoms C(31A), C(31B), C(32A), and C(32B)).

All the non-hydrogen atoms were refined with anisotropic thermal parameters except for those disordered atoms between two sites, which

(13) An XRD of the "pseudo-boehmite" showed it to be fairly amorphous, with intense, broad features corresponding to the peaks associated with boehmite, and minor sharp peaks due to the presence of bayerite. Powder Diffraction File, Inorganic Volume, File Card Nos 21–1307 and 20–11. Joint Committee for Powder Diffraction Standards, Swarthmore, PA, 1990.

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**Table 2.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **1**<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Al(1)	4403(1)	7106(1)	7762(1)	17(1)
Na(1)	4545(2)	1896(2)	9(1)	38(1)
Na(2)	6212(2)	6915(1)	5191(1)	20(1)
O(1)	5328(3)	6641(3)	8699(1)	24(1)
O(2)	5701(3)	5729(2)	7266(1)	20(1)
O(3)	2492(3)	7433(3)	8215(1)	24(1)
O(4)	2953(3)	6733(2)	6786(1)	19(1)
O(5)	5544(3)	9034(2)	7837(1)	24(1)
O(6)	7369(3)	7971(3)	6531(1)	23(1)
O(7)	3919(3)	5431(2)	4196(1)	21(1)
O(8)	3541(3)	7728(2)	5480(1)	20(1)
O(9)	6759(3)	9131(3)	4588(2)	33(1)
O(10)	7807(3)	6189(3)	4131(1)	22(1)
O(11)	2413(3)	10555(3)	8859(1)	28(1)
O(12A)	3969(7)	13750(5)	9174(3)	30
O(12B)	3266(9)	13682(7)	9391(4)	30
O(13)	2531(4)	6736(3)	9657(2)	40(1)
O(14)	3537(3)	9665(3)	10646(2)	40(1)
C(1)	6872(4)	6060(4)	8627(2)	25(1)
C(2)	6614(4)	4986(4)	7821(2)	22(1)
C(3)	969(4)	6958(4)	7672(2)	25(1)
C(4)	1351(4)	7223(4)	6873(2)	23(1)
C(5)	5952(4)	9928(4)	7264(2)	26(1)
C(6)	7547(5)	9558(4)	6959(2)	27(1)
C(7)	2673(4)	6454(4)	4120(2)	22(1)
C(8)	2115(4)	6898(4)	4910(2)	21(1)
C(9)	8050(5)	8940(4)	4107(2)	28(1)
C(10)	7758(5)	7304(4)	3621(2)	24(1)
C(11)	2491(5)	11516(4)	8279(2)	30(1)
C(12)	2359(5)	13173(4)	8639(2)	28(1)
C(13A)	1676(11)	7335(10)	10210(5)	29(1)
C(13B)	1156(9)	7678(8)	9947(4)	29(1)
C(14A)	1930(8)	8575(7)	10765(4)	29(1)
C(14B)	1875(10)	9125(10)	10371(5)	29(1)

<sup>a</sup> *U*(eq) is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

were refined with a common isotropic parameter. For structures **2** and **3**, all hydrogen atoms were refined with isotropic thermal parameters constrained to be 1.2 times the equivalent parameter for the atom to which they were bound; methylene hydrogen atoms were further constrained to calculated positions (C—H 0.97 Å). For **1**, hydrogen atom positions were refined, with three common isotropic thermal parameters: oxygen bound hydrogens, methylene hydrogens on coordinated glycols, and methylene hydrogens on free glycols.

Refinement was by a full-matrix least-squares method based on intensities (SHELXTL-93)<sup>15</sup> with the usual atomic scattering factors and anomalous dispersion corrections;<sup>16</sup> the weights for each reflection were  $[\sigma^2(F_o)^2 + (P_1X)^2 + P_2X]^{-1}$  where  $X$  is  $[(\max(F_o, 20) + 2F_c^2)/3]$ . Final atomic coordinates, bond lengths, angles, and selected torsion angles are given in Tables 2–7. Anisotropic thermal parameters, hydrogen coordinates, and mean plane data (Tables S1–S7) are included as Supporting Information. XRD powder patterns were calculated using DISPOW.<sup>17</sup>

## Results and Discussion

**Synthesis.** The reaction of hydrated alumina with alkaline ethylene glycol was achieved using 1:1, 2:1, and 3:1 Na:Al ratios, by heating the reaction mixture in a distillation apparatus and slowly distilling off the glycol under argon at atmospheric pressure, such that any water produced was immediately removed from the reaction vessel. It was found that if bayerite [Al(OH)<sub>3</sub>] or pseudo-boehmite [AlO(OH)] were used as the

**Table 3.** Selected Bond Lengths (deg) and Angles (deg) for **1** and **2**

	<b>1</b>	<b>2</b> (1) <sup>a</sup>	<b>2</b> (2) <sup>a</sup>
Al(1)–O(1)	1.820(2)	1.860(5)	1.871(5)
Al(1)–O(2)	1.856(2)	1.862(5)	1.858(5)
Al(1)–O(3)	1.849(2)	1.863(5)	1.856(5)
Al(1)–O(4)	1.873(2)	1.818(5)	1.818(5)
Al(1)–O(5)	1.779(2)	1.779(6)	1.771(5)
O(1)–Al(1)–O(2)	87.19(10)	85.5(2)	85.6(2)
O(1)–Al(1)–O(3)	87.79(10)	87.4(2)	86.6(2)
O(1)–Al(1)–O(4)	155.61(11)	149.9(3)	153.8(3)
O(2)–Al(1)–O(4)	86.93(10)	87.6(2)	88.2(2)
O(3)–Al(1)–O(2)	149.78(11)	155.3(3)	150.7(3)
O(3)–Al(1)–O(4)	85.47(10)	86.8(2)	86.5(2)
O(5)–Al(1)–O(1)	99.67(12)	106.6(3)	103.8(3)
O(5)–Al(1)–O(2)	105.18(11)	101.9(3)	104.2(3)
O(5)–Al(1)–O(3)	105.04(11)	102.7(3)	105.1(3)
O(5)–Al(1)–O(4)	104.71(11)	103.5(3)	102.4(3)
Na–O(min)	2.293(6)		2.27(2)
Na–O(max)	2.485(3)		2.506(6)

<sup>a</sup> (1) and (2) refer to the two independent anions. The O atom numbering for **2** includes this as a prefix, thus O(1) becomes O(11) or O(21) in **2**(1) and **2**(2) respectively. Al(1) becomes Al(2) in **2**(2).

source of aluminum, the reaction was much more facile than using corundum or other aluminas and could be completed within 2 h. The products were isolated by reducing the amount of glycol by distillation *in vacuo* followed by addition of dry acetonitrile to precipitate the products as white solids. Repeated washing with dry acetonitrile was necessary to remove residual glycol. Using aluminum triisopropoxide, as the source of aluminum gave products consistent with the formation of identical solutions of aluminoglycolate anions. (See Experimental Section.)

The limited number of analytical techniques available to effectively characterize these compounds led to a heavy reliance on solid state <sup>27</sup>Al NMR and X-ray diffraction methods. Fractional crystallization of the sodium aluminoglycolates was attempted in order to identify the different species present. X-ray quality crystals were formed during fractional crystallizations, by careful addition of acetonitrile to glycol solutions such that the crystals formed over a period of a few days to several weeks.

**Characterization.** Solution NMR studies of the sodium aluminoglycolates proved to be uninformative. Solutions were prepared from the crude material, and the hexagonal crystals were examined. In methanol the compounds rapidly underwent an exchange process, and the only peak observed in the <sup>27</sup>Al NMR spectrum was at 72.9 ppm, characteristic of the tetrahedral aluminate, (MeO)<sub>4</sub>Al<sup>−</sup>. Very little information could be gleaned from running the <sup>27</sup>Al NMR in ethylene glycol solution. No signals were observed except for a small broad hump at *ca* 5 ppm.  $\Delta\nu_{1/2} = 3000$  Hz. Variable temperature NMR up to 90 °C shifted the peak position slightly, to 6.7 ppm, but no significant line narrowing or increased resolution occurred. The solubility of these compounds in other solvents is not sufficient to allow <sup>27</sup>Al NMR solution spectra to be run.

Solid state <sup>27</sup>Al NMR spectra of the crude products invariably showed more than one peak and indicated the presence of aluminum in a variety of coordination spheres, believed to be hexa-, penta-, and tetra-coordinate by comparison with existing data.<sup>18</sup> Previous <sup>27</sup>Al NMR studies reporting pentacoordinate aluminoglycolates have produced materials containing significant amounts of octahedral aluminum.<sup>12,19</sup> It has been postulated that this hexacoordinate aluminum resides at the crystallite surfaces.<sup>19</sup> We have found it a simple process to recrystallize

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**Table 4.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **2**<sup>a</sup>

	x	y	z	U(eq)		x	y	z	U(eq)
Al(1)	2289(3)	5322(1)	2548(1)	34(1)	O(30)	5653(8)	1903(3)	11546(4)	66(2)
Al(2)	3712(3)	310(1)	2392(1)	34(1)	O(31)	10584(8)	1530(4)	7158(5)	79(2)
Na(1)	850(4)	2617(2)	3199(2)	46(1)	O(32)	7601(7)	1229(3)	6372(4)	57(2)
Na(2)	4263(4)	2754(2)	2165(2)	46(1)	C(1)	91(10)	3081(4)	1308(5)	45(2)
Na(3)	4835(4)	2403(2)	8265(2)	46(1)	C(2)	313(10)	2331(4)	1407(5)	48(2)
Na(4)	8200(4)	2258(2)	7126(2)	44(1)	C(3)	4252(9)	2690(4)	6475(5)	45(2)
O(1)	-30(6)	3406(3)	2082(3)	44(1)	C(4)	4057(10)	1942(4)	6376(5)	43(2)
O(2)	1712(6)	2192(3)	1940(3)	44(1)	C(5)	8732(10)	1866(4)	8930(5)	47(2)
O(3)	5645(6)	2819(3)	7009(3)	43(1)	C(6)	8879(10)	2625(4)	9044(4)	44(2)
O(4)	3897(7)	1621(3)	7135(3)	45(1)	C(7)	4565(10)	3140(4)	3956(5)	50(2)
O(5)	7379(6)	1726(3)	8353(3)	45(1)	C(8)	4663(11)	2381(4)	4082(5)	53(2)
O(6)	9106(6)	2931(3)	8297(3)	44(1)	C(9)	-1550(14)	1502(7)	3594(11)	120(5)
O(7)	3303(6)	3292(3)	3346(3)	45(1)	C(10)	-152(13)	1089(6)	3644(8)	89(4)
O(8)	4939(8)	2068(3)	3342(4)	57(2)	C(11)	721(11)	4873(4)	1142(5)	53(2)
O(9)	-1626(8)	2019(4)	3010(5)	89(2)	C(12)	1585(10)	5490(4)	901(5)	50(2)
O(10)	1229(7)	1503(3)	3796(4)	59(2)	C(13)	4360(15)	4898(5)	3813(6)	87(4)
O(11)	1529(6)	4615(2)	1861(3)	40(1)	C(14)	4604(11)	5614(5)	3731(5)	58(2)
O(12)	2233(6)	5840(2)	1611(3)	41(1)	C(15)	-793(11)	5333(5)	3095(6)	68(3)
O(13)	3082(6)	4653(2)	3283(3)	43(1)	C(16)	-689(13)	4986(6)	3933(7)	80(3)
O(14)	3924(6)	5851(3)	2980(3)	46(1)	C(17)	8908(16)	3178(7)	5476(9)	108(5)
O(15)	629(6)	5659(3)	2991(3)	46(1)	C(18)	10369(17)	3067(7)	5187(9)	97(4)
O(16A)	646(19)	4513(7)	4102(11)	57(2)	C(19)	6265(14)	4104(6)	1800(8)	93(4)
O(16B)	154(20)	4387(8)	3794(11)	57(2)	C(20)	5052(13)	4046(6)	1119(7)	80(3)
O(17)	9235(10)	3095(3)	6393(4)	81(2)	C(21)	5439(10)	-124(4)	3749(5)	46(2)
O(18A)	10473(30)	3160(8)	4374(10)	57(2)	C(22)	4471(10)	473(4)	4042(5)	46(2)
O(18B)	9719(24)	3164(6)	4243(8)	57(2)	C(23)	1492(13)	-131(5)	1174(6)	75(3)
O(19)	6621(8)	3477(4)	2191(5)	79(2)	C(24)	1363(12)	614(5)	1219(6)	69(3)
O(20)	3670(7)	3731(3)	1322(4)	56(2)	C(25)	6738(10)	272(5)	1785(5)	59(2)
O(21)	4573(6)	-404(2)	3052(3)	41(1)	C(26)	6569(12)	-91(5)	995(6)	70(3)
O(22)	3748(6)	814(3)	3345(3)	43(1)	C(27)	3941(13)	3951(6)	8740(8)	82(4)
O(23)	2830(6)	-363(2)	1693(3)	43(1)	C(28A)	2524(19)	3521(10)	8864(17)	63(2)
O(24)	2102(6)	864(3)	1957(3)	44(1)	C(28B)	2461(40)	3652(20)	8532(34)	63(2)
O(25)	5354(6)	614(3)	1938(3)	42(1)	C(29)	4146(18)	1983(7)	10254(7)	82(4)
O(26)	5480(10)	-623(4)	968(5)	92(3)	C(30)	5751(15)	1906(5)	10713(8)	88(4)
O(27)	5305(7)	3504(3)	8868(4)	56(2)	C(31A)	10278(20)	867(9)	6843(12)	63(2)
O(28)	2363(7)	3050(4)	8127(5)	73(2)	C(31B)	10301(29)	1106(13)	6388(17)	63(2)
O(29A)	4556(28)	1914(7)	9486(9)	57(2)	C(32A)	8973(20)	939(10)	6121(12)	63(2)
O(29B)	3787(24)	1895(6)	9347(8)	57(2)	C(32B)	8996(33)	679(17)	6450(21)	63(2)

<sup>a</sup>  $U(\text{eq})$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

the crude products of the 2:1 Na:Al reactions in order to isolate the pentacoordinate species.

The first product successfully crystallized, **1**, appeared as chunky needles. The X-ray crystal structure determination shows that the aluminum exists as discrete pentacoordinate glycolato anions in a rectangular pyramidal geometry (Figure 1). Two chelating glycolate ligands form the base of the pyramid, with a monobasic glycolate taking up the fifth position at the apex. An immediate problem apparent with this structure was that an XRD powder pattern generated from the single crystal data showed no similarities with the powder pattern obtained from the crude product mixture. The assumption that this was a minor product and the presence of further signals in the solid state <sup>27</sup>Al NMR spectrum, led to attempts to crystallize further products from the reaction mixture.

A second product from this reaction eventually crystallized from solution as approximately hexagonal plates. An XRD powder pattern of the ground crystals exhibits a distinctive fingerprint which appears as the major component in the XRD of the crude precipitated product. This pattern also appears as a minor component in the XRD patterns of the products of reactions using other Na:Al ratios. The solid state <sup>27</sup>Al NMR spectrum of a sample of the ground crystals shows a single signal appearing at 39 ppm, suggesting that this product contains only pentacoordinate aluminum as in **1**. A single-crystal X-ray structure determination on the hexagonal plates shows the pentacoordinate aluminoglycolate dianion **2** is very similar to **1** described above. The different crystalline forms reflect the different packing arrangements within the cells and the way in which the electrostatic interactions and H-bondings link the

structures together; there is also one additional free glycol per dianion in **2**.

The XRD powder pattern generated from the single crystal data from **2** does not match that obtained from the ground hexagonal plates (Figure 2), although the more intense peaks in the former are present as much less intense peaks in the latter. Preliminary X-ray photographs were taken of several of the crystals prior to full data collection, making it extremely unlikely that a single "rogue" crystal of different composition was chosen for the X-ray structure determination. This implies that yet another phase is formed rapidly during the grinding and packing of the powder sample. <sup>27</sup>Al NMR suggests the pentacoordinate aluminate anions remain intact in the new crystalline phase. The large number and different types of interactions observed between ethylene glycol molecules of crystallization and other atoms in the crystal structures, suggest that they have several alternative, energetically similar positions open to them. This is illustrated by the two crystal structures of **1** and **2** which essentially differ only in their intermolecular contacts. These weak interactions allow the ethylene glycol molecules to be sufficiently mobile, such that on applying pressure, e.g. in the grinding process, they can be perturbed or lost, allowing a (presumably) lower energy crystalline form to be adopted.

The XRD of the ground material suggests that a fraction of it still exists in the crystalline form of the hexagonal plates. Although the conversion is evidently very facile, the process remains incomplete. Further studies of this phenomenon are being completed.

A TGA study in dry air suggests that the ground hexagonal crystals can be formulated as  $\text{Na}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{O})_2(\text{OCH}_2\text{CH}_2-$

**Table 5.** Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **3**<sup>b</sup>

	x	y	z	U(eq)		x	y	z	U(eq)
Al(1)	3430(4)	5210(2)	2733(2)	14(1)	O(26)	9055(12)	5086(5)	4219(4)	38(3)
Al(2)	4847(4)	5875(2)	1836(2)	16(1)	C(1)	6260(14)	4973(6)	2794(6)	19(3)
Al(3)	6541(4)	6989(2)	2250(2)	17(1)	C(2)	5727(14)	4588(6)	3274(6)	22(3)
Na(1)	5352(5)	6334(2)	3349(2)	18(1)	C(3)	828(13)	5145(6)	2050(5)	17(3)
Na(2)	3070(6)	3725(2)	2448(2)	23(1)	C(4)	1754(13)	5486(6)	1643(5)	14(3)
Na(3)	3010(6)	4079(2)	3863(2)	22(1)	C(5)	2106(14)	6121(6)	3376(5)	18(3)
O(1)	5267(8)	5468(4)	2627(3)	11(2)	C(6)	2519(14)	6607(6)	3882(6)	22(3)
O(2)	4216(9)	4510(4)	3081(4)	18(2)	C(7)	5178(14)	5243(6)	822(5)	21(3)
O(3)	1748(9)	4814(4)	2495(4)	17(2)	C(8)	4205(15)	5765(7)	608(6)	31(4)
O(4)	3038(9)	5671(4)	2029(3)	14(2)	C(9)	7724(14)	6198(6)	1493(6)	25(4)
O(5)	3254(9)	5705(4)	3361(4)	16(2)	C(10)	8741(13)	6721(6)	1683(6)	15(3)
O(6)	3750(10)	6934(4)	3749(4)	25(2)	C(11)	4334(14)	7738(6)	2327(6)	23(3)
O(7)	5144(9)	5150(4)	1449(4)	21(2)	C(12)	3640(14)	7112(6)	2134(6)	19(3)
O(8)	4227(10)	6224(4)	1076(4)	22(2)	C(13)	8546(13)	6636(6)	3276(5)	18(3)
O(9)	6760(9)	6201(4)	1930(4)	16(2)	C(14)	8584(15)	6528(6)	3941(6)	27(4)
O(10)	8016(10)	7229(4)	1893(4)	26(2)	C(15A)	131(29)	3415(13)	3342(12)	23(4)
O(11)	5697(9)	7746(4)	2146(4)	17(2)	C(15B)	168(29)	3539(13)	2920(12)	23(4)
O(12)	4753(9)	6650(4)	2263(4)	17(2)	C(16)	-486(16)	4046(7)	3193(7)	41(4)
O(13)	7201(9)	6936(4)	3051(4)	19(2)	C(17)	5809(19)	7783(7)	588(8)	54(6)
O(14)	7508(9)	6110(4)	4066(4)	20(2)	C(18A)	7148(30)	7918(12)	416(12)	23(4)
O(15)	1530(9)	3390(4)	3117(4)	18(2)	C(18B)	6143(30)	8057(13)	76(12)	23(4)
O(16)	522(10)	4539(4)	3425(4)	23(2)	C(19)	2873(16)	3215(7)	1089(6)	30(4)
O(17)	5385(10)	8201(4)	1016(4)	28(3)	C(20)	3201(17)	3898(6)	1065(6)	35(4)
O(18)	7366(12)	8533(4)	261(4)	40(3)	C(21)	2968(17)	8547(7)	3958(7)	40(4)
O(19)	2164(9)	3079(4)	1591(4)	20(2)	C(22)	1566(18)	8382(11)	3605(10)	84(8)
O(20)	4055(9)	4075(4)	1619(4)	25(2)	C(23)	1479(20)	7238(8)	497(7)	54(5)
O(21)	3660(10)	8043(4)	4306(5)	28(2)	C(24)	1322(22)	7929(8)	374(8)	67(6)
O(22A)	640(28)	8305(18)	4035(14)	54(5)	C(25)	4586(14)	5262(6)	4840(6)	20(3)
O(22B)	601(26)	8020(17)	3852(14)	54(5)	C(26)	9472(13)	4808(6)	4813(5)	31(4)
O(23)	2877(11)	7064(5)	410(4)	37(3)	C(30) <sup>a</sup>	576(13)	4475(6)	-188(5)	100
O(24)	2280(15)	8291(6)	832(6)	78(4)	C(31) <sup>a</sup>	2(13)	5001(6)	2(5)	100
O(25)	3488(10)	5025(4)	4373(4)	21(2)	C(32) <sup>a</sup>	-454(13)	4597(6)	485(5)	100

<sup>a</sup> Disordered glycol, see text. <sup>b</sup> U(eq) is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 6.** Selected Bond Lengths ( $\text{\AA}$ ) and Angles (deg) for **3**

Al(1)-O(5)	1.788(9)	Al(3)-O(13)	1.798(9)
Al(1)-O(2)	1.798(9)	Al(3)-O(10)	1.801(9)
Al(1)-O(3)	1.816(9)	Al(3)-O(11)	1.814(9)
Al(1)-O(4)	1.842(8)	Al(3)-O(12)	1.857(9)
Al(1)-O(1)	1.888(9)	Al(3)-O(9)	1.861(9)
Al(2)-O(7)	1.828(9)	Na(1)-O(min)	2.289(10)
Al(2)-O(8)	1.860(9)	Na(1)-O(max)	2.490(9)
Al(2)-O(4)	1.895(9)	Na(2)-O(min)	2.330(10)
Al(2)-O(12)	1.927(9)	Na(2)-O(max)	2.667(9)
Al(2)-O(9)	1.932(9)	Na(3)-O(min)	2.338(10)
Al(2)-O(1)	1.951(8)	Na(3)-O(max)	2.607(10)
O(5)-Al(1)-O(2)	104.2(4)	O(7)-Al(2)-O(1)	91.1(4)
O(5)-Al(1)-O(3)	108.4(4)	O(8)-Al(2)-O(1)	173.1(4)
O(2)-Al(1)-O(3)	91.1(4)	O(4)-Al(2)-O(1)	75.6(4)
O(5)-Al(1)-O(4)	108.4(4)	O(12)-Al(2)-O(1)	87.8(4)
O(2)-Al(1)-O(4)	146.1(4)	O(9)-Al(2)-O(1)	90.8(4)
O(3)-Al(1)-O(4)	87.6(4)	O(13)-Al(3)-O(10)	106.6(5)
O(5)-Al(1)-O(1)	97.5(4)	O(13)-Al(3)-O(11)	105.0(4)
O(2)-Al(1)-O(1)	88.3(4)	O(10)-Al(3)-O(11)	92.7(4)
O(3)-Al(1)-O(1)	153.4(4)	O(13)-Al(3)-O(12)	97.6(4)
O(4)-Al(1)-O(1)	78.4(4)	O(10)-Al(3)-O(12)	154.7(5)
O(7)-Al(2)-O(8)	87.9(4)	O(11)-Al(3)-O(12)	88.0(4)
O(7)-Al(2)-O(4)	97.3(4)	O(13)-Al(3)-O(9)	106.2(4)
O(8)-Al(2)-O(4)	97.8(4)	O(10)-Al(3)-O(9)	87.0(4)
O(7)-Al(2)-O(12)	173.8(4)	O(11)-Al(3)-O(9)	147.4(4)
O(8)-Al(2)-O(12)	93.9(4)	O(7)-Al(2)-O(1)	91.1(4)
O(4)-Al(2)-O(12)	88.3(4)	O(8)-Al(2)-O(1)	173.1(4)
O(7)-Al(2)-O(9)	98.2(4)	O(4)-Al(2)-O(1)	75.6(4)
O(8)-Al(2)-O(9)	96.1(4)	O(12)-Al(2)-O(1)	87.8(4)
O(4)-Al(2)-O(9)	159.5(4)	O(9)-Al(2)-O(1)	90.8(4)
O(12)-Al(2)-O(9)	75.7(4)		

OH)·3.5HOCH<sub>2</sub>CH<sub>2</sub>OH (Figure 3). Loss of a free glycol molecule occurs gradually as the material is heated to 200 °C (requires 13.2% weight loss, observed 13.0%). A second endothermic weight loss at 200–220 °C removes three further molecules of glycol (requires 39.5% weight loss, observed: 40.0%) and results in a species which can be formulated as a

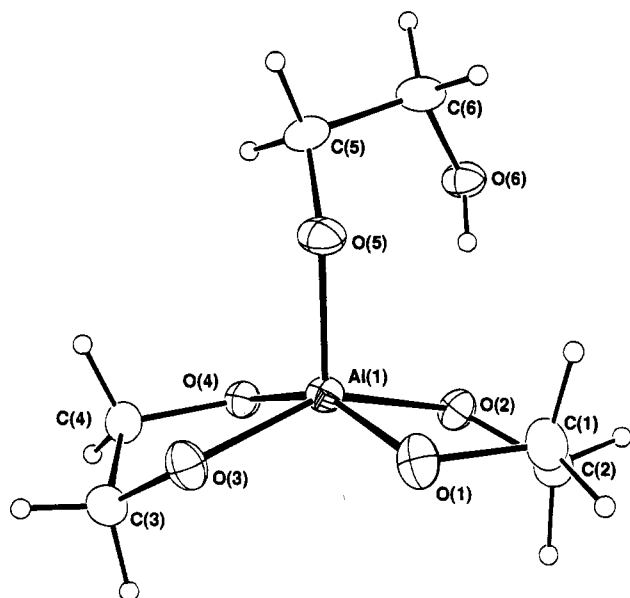
**Table 7.** Selected Torsional Angles

	1	2(1)	2(2)	3
Al(1)-O(1)-C(1)-C(2)	-40.0(3)	38.2(8)	42.6(7)	-29(1)
Al(1)-O(2)-C(2)-C(1)	-25.8(3)	15.6(8)	16.9(8)	-38(1)
Al(1)-O(3)-C(3)-C(4)	-32.1(3)	8(1)	11(1)	34(1)
Al(1)-O(4)-C(4)-C(3)	-33.0(3)	25(1)	28(1)	22(1)
Al(1)-O(5)-C(5)-C(6)	-85.9(4)	92.1(9)	87.3(9)	-162(1)
Al(3)-O(13)-C(13)-C(14)				-166(1)
O(1)-C(1)-C(2)-O(2)	42.0(4)	-34(1)	-38(1)	
O(3)-C(3)-C(4)-O(4)	41.0(3)	-21(1)	-25(1)	
O(5)-C(5)-C(6)-O(6)	65.4(4)	-54(1),	-65(1)	60(1)
		-79(1) <sup>a</sup>		
O(13)-C(13)-C(14)-O(14)				64(1)

<sup>a</sup> Disordered; values for atoms O(6A), O(6B).

dimer by analogy with pentacoordinate silicon species.<sup>3</sup> The weight loss can be explained as a two stage process involving (i) loss of free glycols of crystallization and (ii) dimerization, which results in the loss of a further molecule of glycol per two aluminum atoms. This explanation relies on both processes occurring simultaneously as only a single process is detected in the TGA/DTA traces. The exothermic weight loss at ca. 400 °C can be explained as being due to the total breakdown of the organic species (requires 23.4% weight loss, observed: 23.0%) resulting in the mixed metal oxide 2Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>. The yield of 24.0% compares favorably with a theoretical yield of 24.0%. The high levels of free glycol contained within the crystals, and the apparently ready loss of glycol on grinding, has a large influence on the adoption of molecular orientation within the crystallites.

The product of the 1:1 Na:Al ratio reaction contained mainly tetra-coordinate aluminum, as identified by solid state <sup>27</sup>Al NMR ( $\delta = 50.2$  ppm). Attempts to isolate this complex have thus far been unsuccessful. It was expected that this product would be analogous to the barium aluminoglycolate<sup>11</sup> as the stoichiometry should produce the monoanion; however, the <sup>27</sup>Al NMR

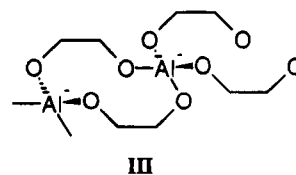


**Figure 1.**  $[\text{Al}(\text{OCH}_2\text{CH}_2\text{O})_2(\text{OCH}_2\text{CH}_2\text{OH})]$  dianion in **1**. Non-hydrogen atoms are drawn with 30% probability ellipsoids.<sup>20</sup>

evidence suggests that this is not the case. C and H microanalytical data show a range of values dependent on the drying conditions. A sample dried at 170 °C *in vacuo* for up to 8 h showed gradual and continual loss of ethylene glycol, resulting in a material approximately corresponding to  $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{O})_{1.6}(\text{OCH}_2\text{CH}_2\text{OH})_{0.8}$ . However, solid state  $^{27}\text{Al}$  NMR still showed the presence of some hexacoordinate aluminum. TGA/DTA studies in nitrogen showed continual endothermic loss of ethylene glycol up to 300 °C. The stoichiometry at this point can be estimated as  $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{O})_2$ . An exothermic weight loss of 52% occurred at 390–400 °C, leaving an oxide of stoichiometry  $\text{NaAlO}_2$ . The theoretical weight loss for the process  $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{O})_2 \rightarrow \text{NaAlO}_2$  is 51.8%.

In looking for likely structures, it may be of use to compare these aluminoglycolates with silicoglycolates. It has been established that tetracoordinate spirocyclic silicates containing chelating 1,2-diolates are energetically unfavorable due to the ring strain associated with the small bite angle of the diolate ligand.<sup>21</sup> Pentacoordinate silicon anions containing chelating 1,2-diolates are much more readily produced due to the decrease in required bite angle in the rehybridized silicon.<sup>22,23</sup> A similar effect is apparent in these aluminoglycolates. While tetrahedral aluminum anions of monodentate alkoxides are readily produced,<sup>24</sup> these studies indicate that the bidentate 1,2-glycolate ligands introduce a ring strain which destabilizes the tetrahedral structure and allows the ready formation of the pentacoordinate dianion. Thus a polymeric structure for the tetracoordinate aluminum species can be postulated by comparison with silicon chemistry<sup>25</sup> and is tentatively proposed as **III**. Dimeric or oligomeric mesomers can be envisaged, and it is likely the isolated product can be formulated within the range bounded by the two extremes  $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OH})_4$  and **III**, as suggested

by the C and H microanalytical data presented above.



A minor product **3** was crystallized out from this 1:1 reaction. This compound exhibits a 3:3 Na:Al ratio, and the anion contains two pentahedral (square pyramidal) aluminums bridged double edgewise by a pseudooctahedral aluminum. The trimer can be described as having two pentahedral dianions, each chelating (via bound glycolate oxygens) a single pseudooctahedral aluminum cation, which contains only one chelating glycolate ligand of its own. The resulting trimeric structure has a net 3-charge which is balanced by three sodium counterions, one of which is encapsulated by the cavity formed by the trimer and its dangling glycolate ligands (Figure 4).

Increasing the Na:Al ratio to 3:1 did not yield the octahedral trimer as hoped,<sup>7</sup> but merely more of the pentacoordinate species **1** described above. The excess sodium present remained in solution and was removed on crystallization of the product.

**Structural Features.** The structures consist of the described five-coordinate anions (Figure 1) in **1** and **2**, trimeric anion (Figure 3) in **3**, sodium cations, and glycol molecules of crystallization, hereafter termed “free”. The intermolecular binding is provided by strong anion-cation interactions through the coordinated and uncoordinated glycol oxygen atoms ( $\text{Na}\cdots\text{O}$  2.27 to 2.61 Å) coupled with hydrogen bonding mainly between the free glycol hydroxyl hydrogen atoms and coordinated oxygen atoms ( $\text{O}-\text{H}\cdots\text{O}$  1.71 to 2.01 Å) but also between the free glycols as well ( $\text{O}-\text{H}\cdots\text{O}$  1.71–2.14 Å) (see Figures 5 and 6).

The two triclinic space group structures **1** and **2** are distinguished by the more extensive hydrogen bonding in **2** between free glycol hydrogens and the coordinated (17 contacts) and uncoordinated oxygen atoms (three contacts) and the sodium cation interactions (Figure 5). In **2** there are no interactions between the four sodium ions and the coordinated oxygens (cf.  $\text{Na}(1)\cdots\text{O}(1)$ , 2.352(2) Å in **1**), and three of the sodium ions ( $\text{Na}(1)$ ,  $\text{Na}(2)$ , and  $\text{Na}(3)$ ) interact *only* with free glycol oxygens. The fourth sodium atom ( $\text{Na}(4)$ ) in **2** has similar intermolecular contacts to  $\text{Na}(2)$  in **1** with one contact to the unbound hydroxyl oxygen on the coordinated glycol, (e.g.  $\text{Na}(2)\cdots\text{O}(6)$ , 2.356 Å in **1**) and five contacts to free glycol oxygens, making up the preferred maximum of six close  $\text{Na}\cdots\text{O}$  contacts found in all the structures.

In **3**, the sodium ions are more closely associated with the coordinated oxygen atoms as shown in Figure 6. The  $\text{Na}(1)$  ion appears to be contained within a pocket made up of six oxygens in the trimeric complex (see Figure 4), interacting with *both* oxygens of the monobasic glycolates (i.e.  $\text{Na}(1)\cdots\text{O}(6)$  2.29(1) Å,  $\text{Na}(1)\cdots\text{O}(5)$  2.42(1) Å,  $\text{Na}(1)\cdots\text{O}(13)$  2.37 Å,  $\text{Na}(1)\cdots\text{O}(14)$  2.44 Å). The other two cations  $\text{Na}(2)$  and  $\text{Na}(3)$  have two close contacts with coordinated glycolate oxygens and four with free glycol oxygen atoms.

Common bonding features in the five-coordinate aluminate anions, including those with bridging oxygens (in **3**) are a shortened Al–O bond to the monobasic glycolate oxygens (Al–O, 1.779(2)–1.798(9) Å, mean 1.783(9) Å) compared with fully coordinated glycolate Al–O bonds (1.798(9)–1.895(9) Å, mean 1.846(28) Å). The shorter Al–O bonds observed for the fully coordinated glycolates consistently involve oxygen atoms with strong intermolecular hydrogen bonds or cation contacts (e.g. Al(1)–O(1) 1.820(2) Å,  $\text{Na}(1)\cdots\text{O}(1)$  2.352(2) Å in **1**; Al(1)–

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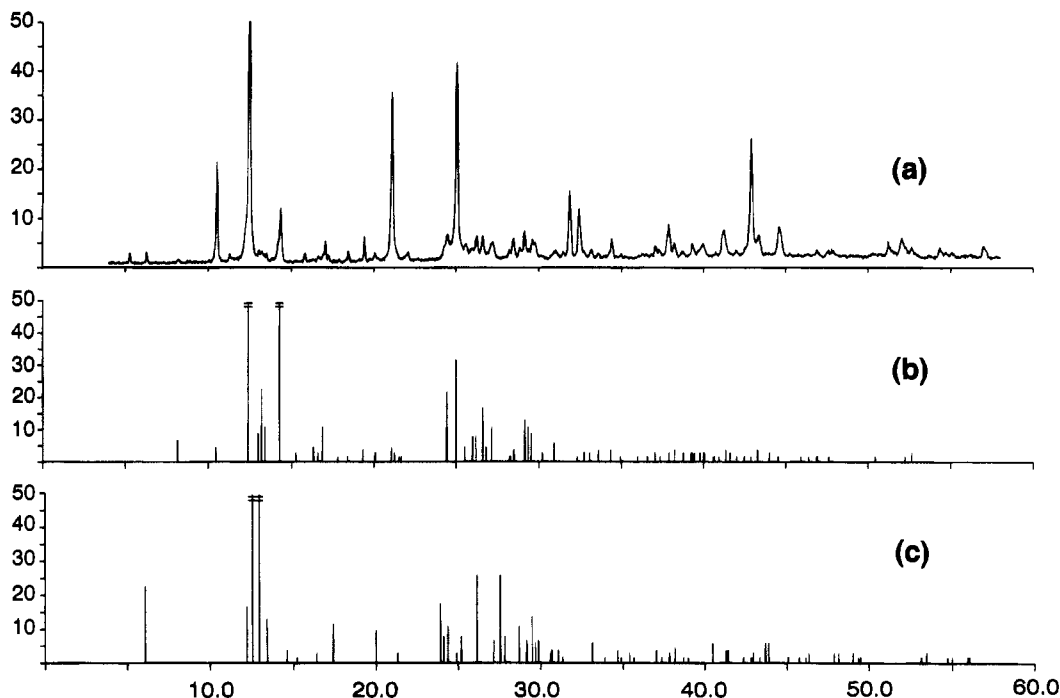


Figure 2. (a) XRD powder pattern of ground crystals of **2**, (b) calculated pattern for **2**, and (c) calculated pattern for **1**.

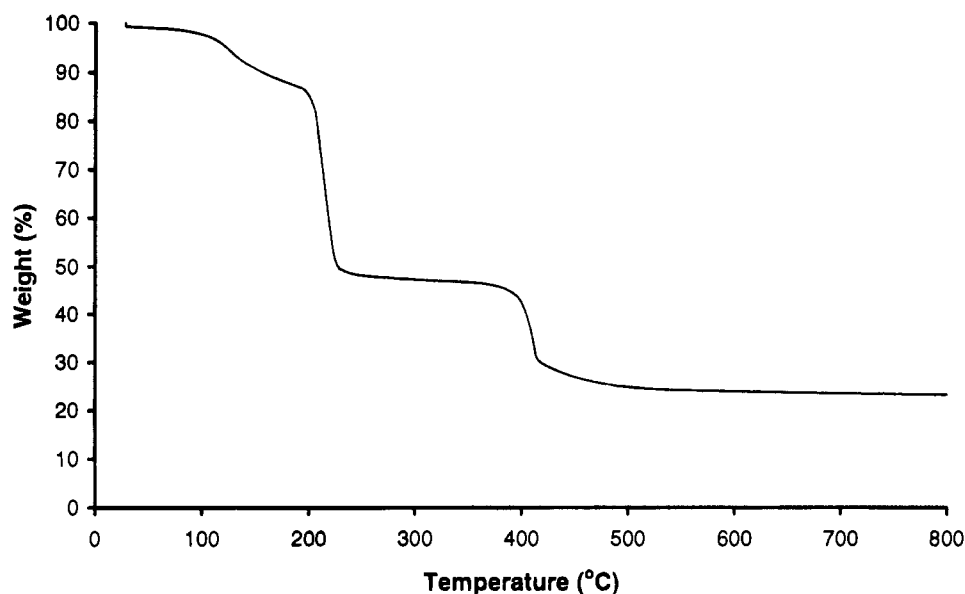


Figure 3. TGA trace of hexagonal crystals of **2** under dry air.

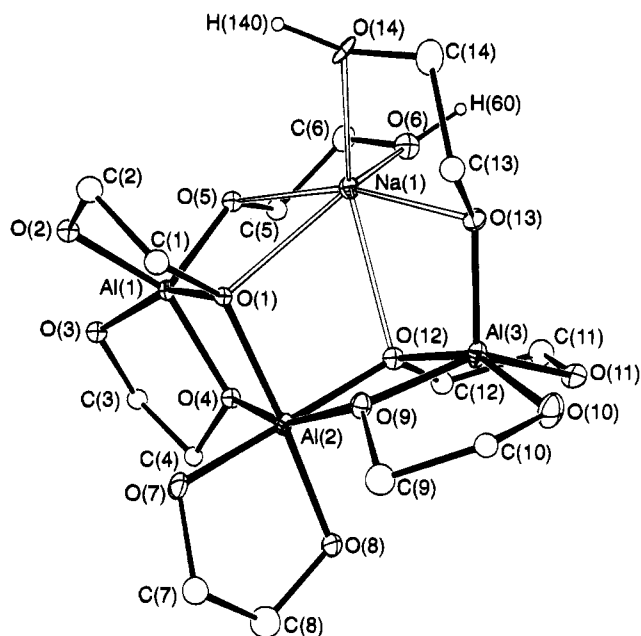
O(14) 1.818(5) Å, O(14)··H(3O) 1.6(1) Å in **2**). The exceptions to this observation occur when short hydrogen bond contacts involve oxygen atoms in bifurcated interactions; for example O(12)··H(27O), H(6O) 1.8(1), 1.6(1) Å in **2**, respectively. There seems to be another factor operating in the trimeric anion in **3**, where bonds to the bridged oxygen atoms are longer than the nonbridged, with for example Al(3)–O(11), O(10) 1.801(9), 1.814(9) Å compared with Al(3)–O(12), O(9) 1.857(9), 1.861(9) Å. These latter bridging Al–O distances are within the range of values observed before.<sup>11,26</sup>

The stereochemistry of the five-coordinated aluminate anions has been investigated using the methods of Muetterties and

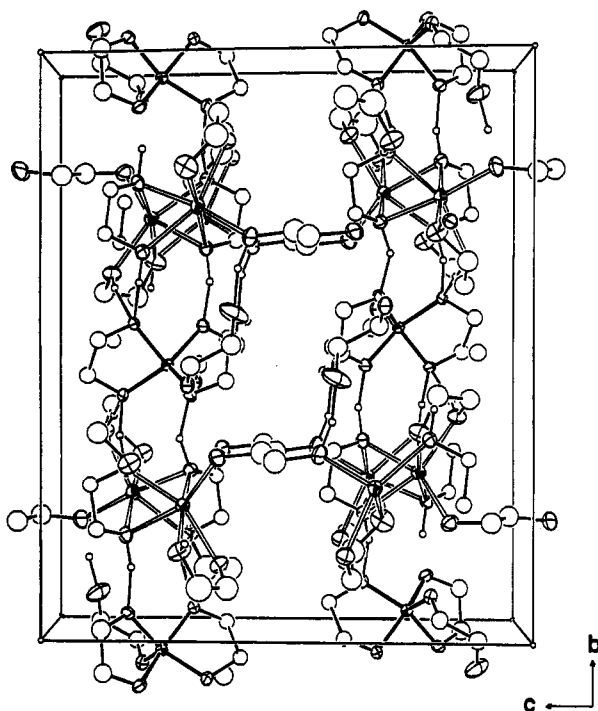
Guggenberger,<sup>27</sup> and the parameters summarized in Table 8. In all cases, the molecules approach the ideal square pyramid in contrast to the trigonal bipyramidal (TBP) structure found in the corresponding silicon analogue,<sup>3,5</sup> and the distorted TBP arrangement observed in the monoanionic aluminate centres of the barium aluminoglycolate polymer.<sup>11</sup> The best pyramid plane in all cases is defined through the oxygen atoms of the chelating glycolates; typical variation from the best mean plane through the four atoms is 0.03–0.06 Å, with the aluminum atoms 0.44–0.47 Å above this plane. Although the two five-coordinate aluminums in the trimeric anion (**3**) are constrained by the shared oxygen atoms with the six-coordinate aluminum, the analysis and mean plane data indicate only minor structural changes are required. The deviations from the mean planes through the oxygens are slightly higher (0.06 Å), but the aluminums are in identical positions above this plane.

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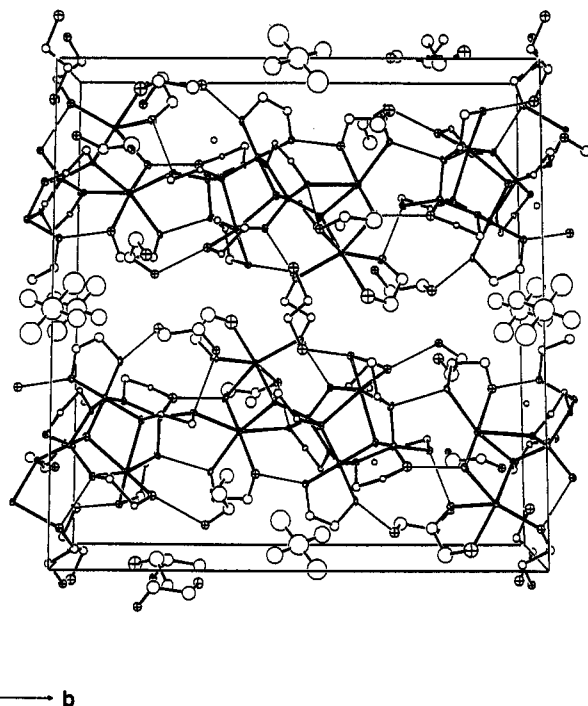


**Figure 4.** Trimeric  $[\text{Al}_3(\text{OCH}_2\text{CH}_2\text{O})_5(\text{OCH}_2\text{CH}_2\text{OH})_2]^{3-}$  anion found in **3**, showing the encapsulated Na(1) cation. All atoms are drawn with 30% probability ellipsoids.<sup>20</sup>



**Figure 5.** Packing of molecules in **2**, viewed down the *a* axis. "Open" bonds: Na...O ionic contacts. Thin bonds: hydrogen bonding. Key: (⊕) oxygen; (○) carbon, hydrogen; methylene hydrogens have been omitted for clarity.<sup>20</sup>

Analysis of the torsional angles in the complexes (Table 7) shows some variation between the three structures (e.g. the Al—O—C—C angles vary from 11 to 40°, with a mean of 29°), but this may reflect the considerable interactions with the cations. This is certainly evident in structure **3** where the monobasic glycolate conformation Al(1)—O(5)—C(5)—C(6) is quite different, and reflects the "encapsulation" of one of the three sodium cations (Na(1)) by O(1), O(5), O(6), O(9), O(13), and O(14) as shown in Figure 4. The six-coordinate aluminum is distorted from pure octahedral geometry by the narrow bite



**Figure 6.** Packing of molecules in **3**, viewed down the *a* axis. Figure specifics are as for Figure 5.

**Table 8.** Shape Angles<sup>a</sup> (deg)

angle	1	2(1) <sup>b</sup>	2(2)	3(1)	3(2)	$D_{3h}$	$C_{4v}$
$e_3$	5.9	3.6	3.2	4.7	5.3	53.1	0
$e_1$	73.2	78.5	74.3	45.3	50.0	53.1	75.7
$e_2$	73.7	78.2	75.1	50.2	46.2	53.1	75.7
$a_2$	76.7	73.4	77.2	55.3	53.7	101.5	75.7
$a_5$	79.0	72.3	76.1	52.8	55.8	101.5	75.7
$a_1$	128.3	120.9	118.4	119.7	130.0	101.5	119.8
$a_3$	128.4	120.4	117.6	91.8	133.8	101.5	119.8
$a_4$	116.2	122.6	119.5	91.6	126.3	101.5	119.8
$a_6$	116.5	122.7	119.4	117.8	124.2	101.5	119.8

<sup>a</sup> Defined in ref 27; the singly bound glycolate oxygen (eg, O(5)) in **1** is taken as the pyramidal atom. <sup>b</sup> (1) and (2) refer to the two independent anions.

angle provided by the bound glycolates, but not in such a systematic way that it can be usefully described as lying between the  $D_{3d}$  and  $D_{3h}$  symmetries.<sup>27</sup>

## Conclusions

Soluble products from the reactions between NaOH, ethylene glycol and alumina have been prepared. The reactions can occur in two different Na:Al stoichiometries, 1:1 and 2:1. A combination of solid state <sup>27</sup>Al NMR and X-ray crystallography shows anionic aluminoglycolates existing in tetra-, penta-, and hexacoordinate geometries. It is proposed that some or all of these species are involved in the incorporation of aluminum in the non-aqueous synthesis of sodalite.

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**Supporting Information Available:** Tables of anisotropic thermal parameters, hydrogen coordinates, and least-squares planes (Tables S1-S7) (10 pages). Ordering information is given on any current masthead page.