Intracage Reactions in Sodalites

Mark T. Weller,* Gordon Wong, Cathy L. Adamson, Simon M. Dodd, and J. James B. Roe
Department of Chemistry, Southampton University, Highfield, Southampton SO9 5NH

Sodalites containing thiocyanate [$Na_8(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$] and nitrite [$Na_8(AlSiO_4)_6(NO_2)_2{\cdot}xH_2O$] have been synthesised by precipitation from aluminosilicate solutions at low temperature. Cation-exchange reactions in aqueous solution were undertaken on the thiocyanate material to afford the fully substituted silver and lithium analogues. The mild and low-temperature conditions under which cation exchange occurs contrast markedly with similar, previously described reactions on this family of compounds involving melts and direct reaction between solids at 300—800 °C. These compounds undergo slow intracage oxidation reactions of the anions on heating in air to yield sodalites containing OCN^-, S_x^-, and SO_4^{2-} from SCN^- and NO_3^- from NO_2^-. The extent and direction of these oxidation reactions depends upon the nature of the cation also present in the cage. The products of these indirect syntheses have been characterised by power *X*-ray and neutron diffraction, i.r. and u.v.–visible spectroscopy, and thermogravimetric analysis.

Sodalites are an unusual group of aluminosilicates in that they contain within the framework anionic species such as Cl^-, SO_4^{2-}, and SCN^-. They are of the general formula $M_8(AlSiO_4)_6X_2$ where M may be sodium, lithium, potassium, silver, or more rarely other monovalent or divalent cations, and X_2 represents anions of overall charge 2^-. Structurally, they are based upon a cubo-octahedral cage linked in three dimensions and may be considered to consist of an inorganic salt (2MX) embedded in a sodium aluminosilicate ($6MSiAlO_4$). Sodalites prepared by solid-state reaction at high temperatures are anhydrous, while materials synthesised by precipitation at low temperature from aqueous solutions are hydrated, though the water is readily lost above 200 °C.

Sodalites, and to a lesser extent cancrinites, have been the subject of a number of recent structural studies[1–5] in which detailed information regarding framework and cavity-ion positions has been obtained. This family of compounds is of interest in terms of their photochromic, cathodochromic, and ferroic properties.[6] The structure of ultramarines has been studied[7] and found to be based upon sodalite but with polysulphide species (S_x) constituting the cavity anions. The reaction by which S_x^- is formed in the sodalite cage is thought to involve the initial formation of a colourless ultramarine which then reacts with sulphur dioxide to give coloured materials.

Relatively little is known about the thermal stability of complex anions contained within the sodalite cages and with this in mind a series of thermal decomposition experiments was carried out using thermogravimetric analysis (t.g.a.) in conjunction with i.r., u.v.–visible, *X*-ray diffraction, and neutron diffraction. Materials chosen for study included the thiocyanate derivatives; Hund[8] has reported that heating $Na_8(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$ resulted in a blue material generally indicative of the formation of an ultramarine $Na_8(AlSiO_4)_6S_x$. This method would be of interest as a technique for preparing crystalline ultramarines as direct high-temperature methods frequently result in poorly crystalline compounds.[7] Given that the S_2^-/S_3^- ions are stabilised by enclosure in an aluminosilicate cage by preventing combination to S_4^-, it would seem likely that the stability of other species could also be altered by incorporation in sodalites.

Results

The parent sodalite materials, $Na_8(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$ and $Na_8(AlSiO_4)_6(NO_2)_2{\cdot}xH_2O$ were synthesised by precipitation from aqueous solution and subsequent ion-exchange reactions on the thiocyanate derivative were undertaken. These unheated products are summarised in Table 1.

Table 1. Parent and ion-exchanged sodalites with refined cell parameters (x = 1—2)

Material	Refined cell constant, a_0, (Å)
$Na_8(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$	9.086(2)
$Li_8(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$	8.645(7)
$Ag_xNa_{8-x}(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$	9.057(2)
$K_{0.38}Na_{7.62}(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$	9.186(2)
$Na_8(AlSiO_4)_6(NO_2)_2{\cdot}xH_2O$	8.906(1)

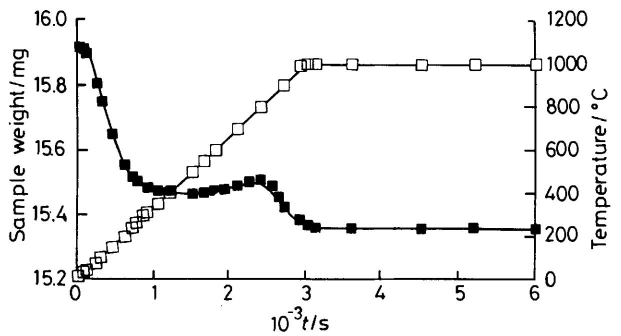

Figure 1. Thermogravimetric trace for a sample of $Na_8(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$ heated in air at 20 °C min^{-1}: (■), sample weight; (□), temperature

Thermal Behaviour of $Na_8(AlSiO_4)_6(SCN)_2{\cdot}1.6H_2O$.—Initial thermogravimetric data, Figure 1, were collected from a sample heated in air to 1 000 °C at 20 °C min^{-1}. A complex behaviour is observed in which a series of independent weight gains and losses occurs; the initial major weight loss is that of water and was consistent with the formula $Na_8(AlSiO_4)_6(SCN)_2{\cdot}1.6H_2O$. In order to investigate the reactions occurring at higher temperatures and characterise the intermediate products a series of different thermal treatments was undertaken, as summarised in Table 2.

Table 2. Summary of thermal treatments and products

Furnace temperature/ °C	Time/ min	Cell constant/ Å	Colour	I.r. band intensity ratio 2 070:2 170 cm^{-1}
Unheated	0	9.086(2)	White	2 070 cm^{-1} only
400	45	9.053(2)	White	6:1
600	45	9.082(2)	Pale blue	4:1
800	45	9.069(2)	Turquoise	2:1
900	10	9.032(1)	Green	2:1
900	60	9.031(1)	Green	1:2
900	315	9.051(2)	Blue	No band
900	1 440	9.046(1)	White	No band
900	2 850	9.073(1)	White	No band

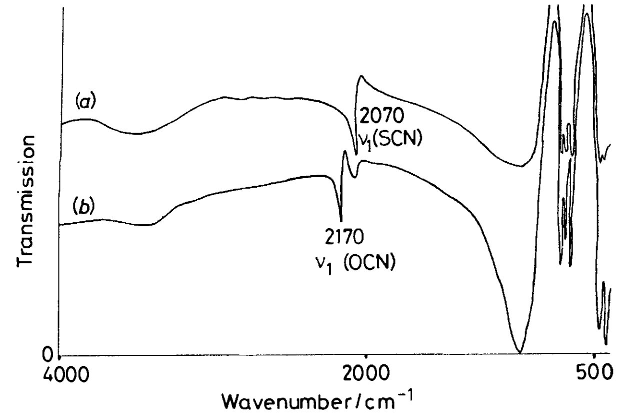

Figure 2. Infra-red spectra of (*a*) $Na_8(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$ unheated and (*b*) $Na_8(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$ heated in air at 900 °C for 60 min

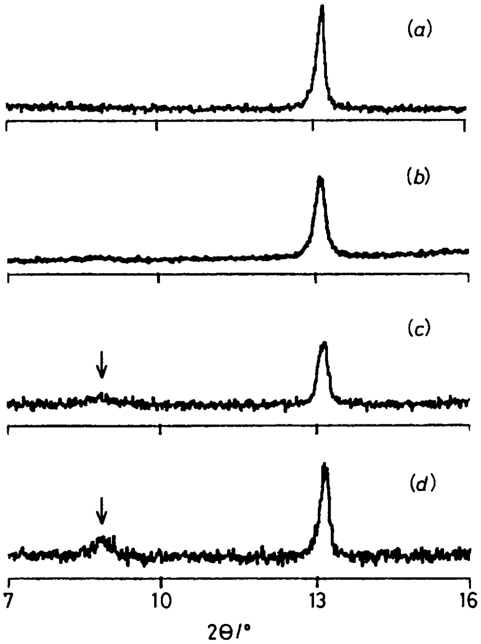

Figure 3. Typical low-angle powder *X*-ray diffraction data from $Na_8(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$ heated at 900 °C for (*a*) 60 min, (*b*) 300 min, (*c*) 12 h, and (*d*) 24 h respectively. The developing (100) reflection is arrowed; the major peak is the (110) reflection

The decomposition of the Na/SCN sodalite occurs in several stages which can be easily monitored by i.r. spectroscopy. Table 2 shows the ratio between the i.r. bands at 2 070 (band A) and 2 170 cm^{-1} band B as a function of the severity of heating. It was found that bands due to the aluminosilicate framework were relatively unaffected by the various heating processes indicating that the sodalite structure was essentially preserved throughout. These i.r. bands were assigned to the C≡N stretch of SCN and OCN respectively. Initially the intensity of band A was observed to decrease with heating, while B increased showing a gain of OCN at the expense of SCN (Figure 2). This process continues until both bands disappear after prolonged heating at higher temperatures.

Heated materials displayed marked colour changes from the white of the original Na/SCN sodalite to various shades of green and blue; to study this more closely a number of the coloured samples were subjected to solid-state u.v.–visible reflectance spectrometry in an attempt to pinpoint the species responsible for the colours.

Electronic spectroscopy. Previous work on structurally related compounds[9,10] has established the presence of, amongst other chromophores, S_3^- and/or S_2^- and confirmed these as being partly or wholly responsible for the bright colours observed in materials such as ultramarine blue, green, violet, and pink. The ratio between S_3^- and S_2^- was found to be important to the colour observed and since the heated products in the current work displayed colours ranging from green-blue through to dark blue it was decided to determine whether S_3^- and/or S_2^- were similarly responsible for the colours seen in the heat-treated materials.

U.v. spectra were recorded between 850 and 190 nm using either barium sulphate or magnesium oxide as a matrix reference material. Clark and co-workers[9,10] have observed bands at 600 and 370 nm characteristic of $S_3^-(^2B_1 \longleftarrow {}^2A_1)$ and $S_2^-(^2\pi_{\frac{3}{2}u}, {}^2\pi_{\frac{1}{2}u} \longleftarrow {}^2\pi_{\frac{3}{2}g})$ respectively; in the current work, bands were also observed at similar wavelengths, confirming the presence of both species.

For materials heated for approximately 5 min at 900 °C the observed S_3^-:S_2^- ratio was found to be approximately 1:1. Materials heated for gradually longer times gave a progressively larger ratio (2.6:1 after 5 h at 900 °C); the absorption band of S_3^- lies at 600 nm while S_2^- lies at the shorter wavelength of 390 nm. The combination of S_3^- and S_2^- in different ratios hence results in the colours observed, from green-blue for S_3^-:S_2^- 1:1 to dark blue for S_3^-:S_2^- 2.6:1, plus various intermediate shades. Materials subjected to prolonged heating (24 h at 900 °C) returned to the original white colour and u.v.–visible spectroscopy confirmed the absence of S_3^- and S_2^-.

X-Ray diffraction. The decomposition processes occurring in the system were monitored closely by *X*-ray diffraction. The parent Na/SCN sodalite gave a primitive cubic pattern typical of a sodalite structure while heated products were found to give essentially identical patterns also indexable on a cubic unit cell, but with small shifts in diffraction peak positions. The basic sodalite structure was therefore preserved on heating. Lattice constant values were refined from each data set using a least-squares method (Table 2); the general behaviour reflects an initial contraction of the cell constant as water is lost (at short heating times or low temperatures) followed by irregular changes at higher temperatures/longer heating times. This is probably associated with complex changes in the type of species contained in the cavity, *i.e.* OCN, SCN, and S_n and their proportions. A significant change observed was the appearance of the (100) and the (111) peaks in the white materials obtained at the highest temperatures, indicating a change in cell symmetry from a sodalite-like phase to a noselite-like one. In noselites the anions are divalent and only half the cages are occupied with the resultant absence of the glide-plane element. This was found to be the case for materials heated for long times beyond the 'blue stage' and which had regained the white colour (Figure 3). The final white decomposition product was shown to be $Na_8(AlSiO_4)_6SO_4$ by its *X*-ray lattice parameter, 9.073 Å, close to that expected for this material (9.067)[11] and a positive spot test for sulphate on a solution obtained by dissolution of the solid in dilute hydrochloric acid.

The likely decomposition route for Na/SCN sodalite is summarised in the Scheme. However, it is worth noting that the actual progress of the reaction depends markedly upon the heating rate as all the stages are relatively slow relying on migration of species in and out of the lattice.

$Na_8(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$	white
$\downarrow$ 200 °C	
$Na_8(AlSiO_4)_6(SCN)_2$	white
$\downarrow$ 500 °C	
$Na_8(AlSiO_4)_6(SCN,OCN,S_3^-,S_2^-)$	blue-green
$\downarrow$ 600 °C	
$Na_8(AlSiO_4)_6(S_3^-,S_2^-)$	blue
$\downarrow$ 850 °C	
$Na_8(AlSiO_4)_6SO_4$	white

Scheme.

Thermal Behaviour of $K_xNa_{8-x}(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$ *and* $Li_xNa_{8-x}(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$.—A series of thermal treatments (600—800 °C) was undertaken to investigate the decomposition behaviour of these exchanged derivatives. Potassium-exchanged materials gave virtually identical thermal characteristics to Na/SCN sodalite as expected from the low level of exchange of Na by K.

The decomposition of $Li_8(AlSiO_4)_6(SCN)_2{\cdot}xH_2O$, subjected to heating in the temperature range 600—800 °C, occurred in an analogous fashion to that of Na/SCN sodalite except the colours observed were mainly pale grey/blue. Prolonged heating led to a white product containing sulphate, *i.e.* $Li_8(AlSiO_4)_6SO_4$. Extended treatments at intermediate temperatures (650 °C) gave no appreciable change in material, except loss of water, and the onset temperature for decomposition of SCN was found to occur at above 700 °C. U.v. reflectance spectra recorded from the coloured intermediate decomposition products formed at 700 °C showed similar features to those obtained with the sodium analogues, however the bands were much weaker indicating that the level of S_2^- and S_3^- was much lower in the presence of lithium.

Thermal Behaviour of $Ag_xNa_{8-x}(AlSiO_4)_2(SCN)_2{\cdot}xH_2O$.—A series of heat treatments between 600 and 800 °C was carried out showing no change in composition up to 650 °C. Higher temperatures were found to effect relatively rapid collapse of the structure until virtually no sodalite phase remained in the *X*-ray diffraction pattern (800 °C, 30 min, air); the principal product of decomposition was found to be silver metal which was readily indexed upon a cubic close-packed unit cell (4.094 Å). Infra-red spectroscopy showed the absence of both SCN and OCN and confirmed the sodalite framework to be significantly decomposed at 800 °C. The colour of the intermediate decomposition product formed at 650 °C was markedly different from that of the sodium-based analogue with dark green/brown being most prevalent. U.v.–visible spectra obtained showed a strong absorption at approximately 400 nm indicative of S_2^- however there was little evidence for the presence of S_3^-.

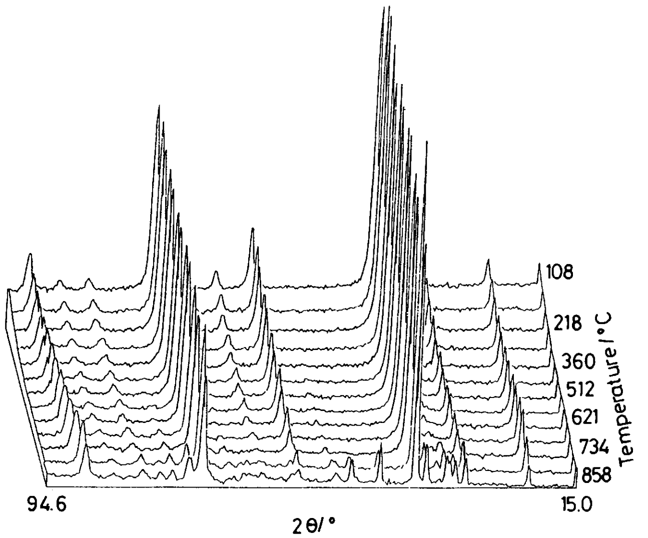

Figure 4. Powder neutron diffraction data as a function of temperature for $Na_8(AlSiO_4)_6(NO_2)_2{\cdot}xH_2O$. Additional phases only appear above 750 °C

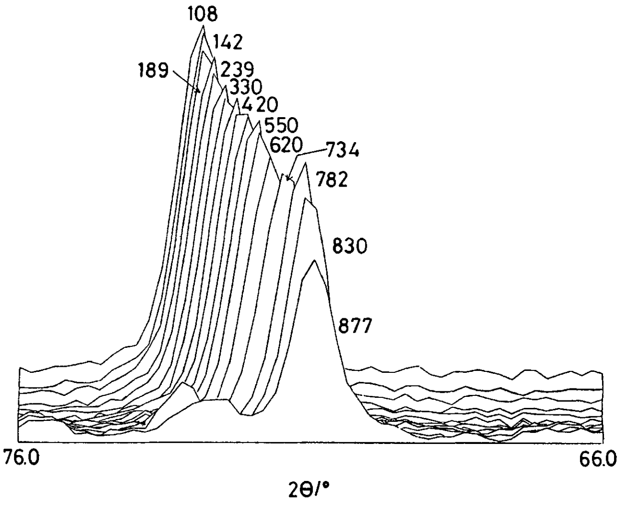

Figure 5. Position of the (330) peak of $Na_8(AlSiO_4)_6(NO_2)_2{\cdot}xH_2O$ as a function of temperature (°C) (neutron diffraction data)

Thermal Behaviour of $Na_8(AlSiO_4)_6(NO_2)_2{\cdot}xH_2O$.—As for the Na/SCN sodalite system the thermal behaviour was studied initially using a thermogravimetric balance. A typical profile showed a small initial weight loss as water, followed by a slow mass increase above 600 °C; products obtained at various heating rates (5—20 °C min^{-1}) to *ca.* 900 °C showed no sign of any colour change. Unheated Na/NO_2 sodalite gave a simple powder *X*-ray diffraction pattern indexable on a cubic lattice constant of 8.906 Å. Heating to temperatures of around 650 °C/700 °C for short times (*ca.* 45 min) produced no major change in pattern, while heating to $\geqslant$900 °C resulted in the appearance of some impurity phases, assignable to $NaAlSiO_4$ and $NaAlSi_3O_8$.

Variable-temperature powder neutron diffraction data, shown in Figures 4 and 5, were collected on a sample of Na/NO_2 sodalite and showed no phase change up to around 750 °C; beyond this temperature a number of weak impurity phases appeared at the expense of sodalite peaks. An overall expansion of the unit cell occurs with increasing temperature as

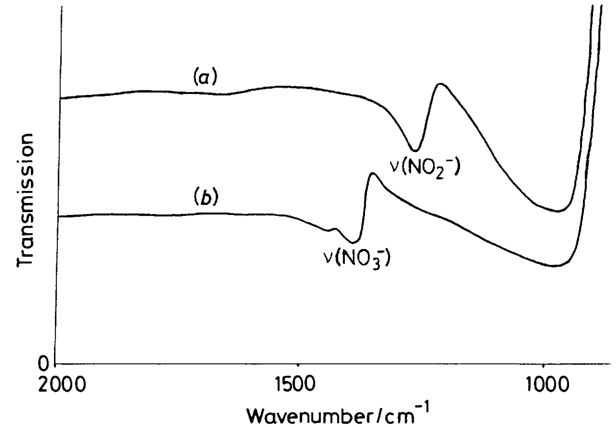

Figure 6. Infra-red spectra of (*a*) $Na_8(AlSiO_4)_6(NO_2)_2 \cdot xH_2O$ unheated and (*b*) $Na_8(AlSiO_4)_6(NO_2)_2 \cdot xH_2O$ heated to 650 °C for 30 h

would be expected. However, this rate of increase is not constant, indeed there is a marked expansion in the temperature range 500—650 °C which would be consistent with the introduction of a larger species into the sodalite cage.

A series of materials was heated at moderate temperatures (650 °C) for different times and powder *X*-ray diffraction and i.r. spectroscopy were used to monitor any changes (Figure 6). Framework bands dominate the i.r. spectra below 1 100 cm^{-1}; the major band assignable to cavity anion modes is the ν_3 N=O stretch of NO_2^- at *ca.* 1 270 cm^{-1}. Heating at 650 °C in air resulted in the growth of bands at *ca.* 1 390 at the expense of the NO_2^- band at 1 270 cm^{-1}. The frequencies of these new bands are consistent with those expected from nitrate and a similar feature is present in the i.r. spectrum of nitrate cancrinite.[12] Thus NO_2^- is slowly oxidised to NO_3^- at 650 °C without collapse of the sodalite framework and in air at 650 °C the oxidation of NO_2^- is virtually complete after 30 h. This formation of NO_3^- from NO_2^- also allows interpretation of the variable-temperature neutron diffraction data with the faster expansion of the sodalite cage above 500 °C as the larger nitrate ion is formed from nitrite. We are at present trying to model the changes in the neutron diffraction data on such a reaction.

For comparison, materials were heated in flowing N_2, also at 650 °C, for various lengths of time. As before, no appreciable decomposition occurs at this temperature, even on prolonged heating. I.r. spectra showed no change within the wavenumber range 1 000—1 500 cm^{-1} demonstrating that no conversion of nitrite into nitrate had occurred in the absence of oxygen, even after heating for 3 d.

Conclusions

Previous work has demonstrated that the cations in sodalites may be readily exchanged at high temperatures for example sodium by silver using silver salt melts at approximately 300 °C or sodium by lithium by reaction with lithium salts above 600 °C. However, such extremes of reaction conditions have been shown to be unnecessary and sodium may be replaced by lithium and silver from aqueous solutions rapidly at 100 °C. This replacement occurs with the expected contraction of the sodalite cage when lithium replaces sodium. The ease of cation exchange reflects the size of the intercavity bottlenecks in the sodalite structure, approximately 1.74 Å permitting rapid passage of small cations between neighbouring cages. Anion exchange is considerably more difficult although replacement of chloride by sulphate has been reported.[13] However, oxidation of the cavity species can occur above approximately 500 °C indicating that transport of oxide ions through the sodalite structure is possible. Such behaviour occurs more readily than decomposition of the sodalite structure to a condensed aluminosilicate, *e.g.* nepheline $NaAlSiO_4$ and liberation of the trapped inorganic salt which only occurs above 800 °C. This allows the preparation of unusual/unstable species in the cavity such as S_n^-. Direct synthesis of nitrate sodalites under aggressive hydrothermal conditions has been reported;[12] however the current work shows that such compounds may be prepared by a two-stage reaction involving nitrite sodalites as an intermediate.

The nature of the in-cage reaction is also controlled by the cations present. Diffusion of species in and out of the sodalite cages seems relatively facile in the sodium compounds. However, in the lithium derivatives a substantial contraction of the sodalite framework occurs reducing the intercavity bottleneck size. This leads to higher temperatures for the decomposition reaction of the thiocyanate groups and greater difficulty in preparing materials containing high proportions of polysulphide anion radicals. In the silver-exchanged compounds the formation of S_2^- is preferred over that of S_3^-.

The ability of small species to diffuse through the sodalite structure is probably important during the manufacture of ultramarines. In this synthesis it seems likely that a colourless polysulphide sodalite is the initial product at high temperatures and this undergoes a secondary in-cage reaction producing the coloured polysulphide radical anions *in situ* by heating in SO_2 at about 500 °C. This ability to form reactive species in the sodalite cage where they are hindered from further reaction should permit the in-cage synthesis of other unusual inorganic species.

Experimental

Sodalites were synthesised using a solution method in which a mixture of sodium silicate and the required cavity salt (anhydrous NaSCN, $NaNO_2$) was added to a sodium aluminate solution according to the method of Hund.[8] Refluxing at 110 °C for 24 h gave the required material, in each case as a fine white powder which was washed and dried at 110 °C. Compounds synthesised in this manner were $Na_8(AlSiO_4)_6(SCN)_2 \cdot xH_2O$ (Na/SCN sodalite) and $Na_8(AlSiO_4)_6(NO_2)_2 \cdot xH_2O$ (Na/NO_2 sodalite).

Ion Exchange.—Ion exchange of Na/SCN sodalite was carried out in aqueous solutions of KCl and LiCl. Sodium thiocyanate sodalite (*ca.* 10 g) was added to a solution of lithium chloride (5 mol dm^{-3}) and the mixture refluxed at 100 °C for 24 h. The product was filtered off and washed thoroughly with distilled water. The stoicheiometry was determined by flame photometry after dissolution in dilute hydrochloric acid and showed complete exchange of sodium by lithium. Less concentrated solutions and shorter reaction times were found to produce only partially exchanged materials. As expected, Li/SCN sodalite gave a smaller cell constant (8.645 Å) than its sodium analogue (9.086 Å) a degree of contraction similar to that observed in other sodalites where sodium is completely replaced by lithium.

Exchange of sodium by potassium was performed in an analogous manner using an aqueous solution of potassium chloride (5 mol dm^{-3}). However, the degree of sodium replacement was limited as has been found previously in other sodalites,[11] a result of the sodalite framework being unable to expand sufficiently to accommodate a high proportion of the large potassium ions. Flame photometry gave a stoicheiometry of $K_{0.38}Na_{7.62}(AlSiO_4)_6(SCN)_2 \cdot xH_2O$ and *X*-ray diffraction traces for potassium-substituted materials displayed significant shifts in peaks to lower 2θ values, reflecting the expansion in cage expected for the incorporation of a proportion of the larger cation. Silver-ion exchange was performed using $AgNO_3$ (5.6 mol dm^{-3}). Silver-ion content was determined by dissolution in acid and volumetric analysis. The exchanged khaki material gave a cubic sodalite *X*-ray diffraction pattern which was indexed and refined to give a cell constant value (9.057 Å).

Washed and dried compounds were characterised primarily by *X*-ray diffraction using a position-sensitive detector-based system (nickel-filtered Cu-K_{α_1} radiation, $\lambda = 1.5406$ Å); each data set was indexed according to a simple cubic sodalite structure and refined using a least-squares method to yield the cell parameter.

Materials were heated to elevated temperatures either in recrystallised alumina crucibles or in a platinum crucible as part of the thermogravimetric analysis equipment. The latter comprised a Stanton Redcroft TG1000 system incorporating a microfurnace attached to a thermobalance and chart recorder for graphical output; weight measurements accurate to 1 µg were achieved. I.r. data were collected over the ranges 4 000—200 cm^{-1} (Perkin-Elmer PE599) and 4 000—500 cm^{-1} (Perkin-Elmer PE1600 FTIR) as pressed 13-mm KBr or CsI discs to monitor changes in cavity bands with heating. Variable-temperature powder neutron diffraction profiles were obtained using the D1B instrument at the Institut Laue–Langevin (I.L.L.) (Grenoble, France). Samples (*ca.* 10 g) were enclosed in silica tubes and heated at *ca.* 2 °C min^{-1} to *ca.* 950 °C and data were collected in the angular range 5—95 °C at a wavelength of 2.52 Å every 3 min. Solid-state u.v.–visible spectroscopy was performed using a Perkin-Elmer PE554 spectrometer.

Acknowledgements

The authors thank the S.E.R.C. for grants associated with this work and a studentship for G. W. Thanks are also due to the S.E.R.C. and the I.L.L. (Grenoble) for the provision of neutron beam facilities.

References

1 W. Depmeier, *Acta Crystallogr., Sect. B, 1988,* **44**, 201.
2 S. Luger, J. Felsche, and P. Fischer, *Acta Crystallogr., Sect. C*, 1987, **43**, 1.
3 M. Danø, *Acta Crystallogr.*, 1966, **23**, 434.
4 V. J. Löns and H. Shulz, *Acta Crystallogr.*, 1967, **23**, 434.
5 I. Hassan and H. D. Grundy, *Acta Crystallogr., Sect. B*, 1984, **40**, 6.
6 I. F. Chang, *J. Electrochem. Soc.*, 1974, **121**, 815.
7 S. E. Tarling, P. Barnes, and J. Klinowski, *Acta Crystallogr., Sect. B*, 1988, **44**, 128.
8 F. Hund, *Z. Anorg. Allg. Chem.*, 1984, **511**, 225.
9 R. J. H. Clark and M. L. Franks, *Chem. Phys. Lett.*, 1975, **34**, 69.
10 R. J. H. Clark and D. G. Cobbold, *Inorg. Chem.*, 1978, **17**, 3169.
11 D. Taylor, *Contrib. Mineral. Petrol.*, 1975, **51**, 39.
12 R. M. Barrer, J. F. Cole, and H. Villiger, *J. Chem. Soc. A*, 1970, 1523.
13 L. T. Todd, C. E. Stroud, and E. F. Farnell, *Mater. Res. Bull.*, 1980, **15**, 595.

Received 20*th July* 1989; *Paper* 9/03072G