

ALUMINATE SODALITES - A FAMILY OF INCLUSION COMPOUNDS WITH
STRONG HOST-GUEST INTERACTIONS

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Aluminate sodalites belong to a structural family which, in principle, has been known for quite a long time and which is closely related to various zeolites. Naturally occurring sodalites belong to the class of aluminosilicates (e.g., sodalite in the proper sense has the idealized formula $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$), whereas aluminate sodalites have a composition $\text{M}_8[\text{Al}_{12}\text{O}_{24}](\text{XO}_4)_2$ for a (pseudo-)cubic cell ($a_0 \sim 9.5\text{\AA}$), with $\text{M}=\text{Ca}, \text{Sr}, \dots$ and $\text{X}=\text{S}, \text{Cr}, \text{Mo}, \text{W} \dots$

In comparison with other inclusion compounds dealt with in these Proceedings, aluminate sodalites have a remarkable thermal stability. The usual preparation, by sintering appropriate mixtures of the corresponding oxides, requires temperatures of as high as 1350°C , whereas melting temperatures seem to be around 2000°C . Structural work and measurements of physical properties have not been possible until a technique of growing "single crystals" by the flux method had been developed. This technique works at about 1100°C and, because of the occurrence of phase transitions below these temperatures, the "single crystals" thus obtained are usually twinned.

The structure is characterized by corner-connected AlO_4 tetrahedra, the centres of which occupy the vertices of an - ideally - regular truncated octahedron. This is the so-called sodalite cage. The sodalite framework is then formed by joining together the sodalite cages in a body-centred arrangement, thereby filling the available space completely (the regular truncated octahedron is a space-filling polyhedron). The framework -it can be regarded as the host- is quite open and accommodates in its cavities the guests, viz. the so-called cage anions XO_4 and the cage cations M. The former occupy the centres of the sodalite cages, whereas the latter are situated near, but not necessarily at, the centres of the six-membered rings shared between two adjacent cages. Fig. 1 illustrates some particularities of the

sodalite structure.

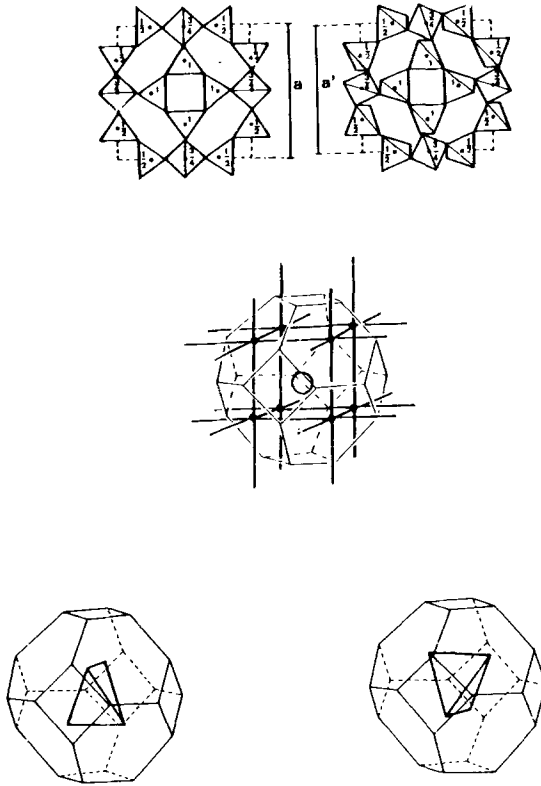


Fig. 1: Some particularities of the sodalite cage:
 Top: Upper half of the sodalite (after ref. 9);
 fully expanded (left) and partially collapsed
 (right hand side).
 Middle: The cage cations (small black circles)
 form a framework (thick solid lines) which interpen-
 etrates the sodalite framework (truncated octahedron,
 thin lines). The cage anions (big circle) occupy

the centre of the sodalite cage.

Bottom: Aluminate sodalites contain tetrahedral cage anions; these are oriented in such a way that their vertices (O atoms of the cage anions) point at the midpoints of some edges of the truncated octahedron (= framework O atoms). Two possible orientations are shown.

The AlO_4 tetrahedra are far from being ideal. The degree of distortion is, however, constant for the whole family of aluminate sodalites, as it is for any family of constant framework composition. An explanation has been proposed [1] for this intrinsic strain as being the result of an attempt of the framework to avoid an unfavourable conformation, required by its proper topology. The sodalite framework has the remarkable property of being quite flexible via cooperative rotations of the tetrahedra (so-called tilts, cf. fig. 1 and refs. 1,2). The flexibility enables the framework to adjust its size to that of the guest species via "partial collapse" [2]. Furthermore, the framework does not only adjust itself to the sizes, but also - in a certain sense, to the shape of the species [3]. This is shown schematically in Fig. 1. A tetrahedral cage anion within the sodalite cage is oriented in such a way that its O atoms at the vertices point at O atoms of the framework, rather than pointing into the direction of the threefold axes of the sodalite cages. The framework O atoms are repelled by this interaction and the cage is deformed. An important consequence is that the cubic symmetry of the structure is destroyed. By the repulsive interactions between the O atoms of the host and the guests several phenomena are produced which might be of interest for chemists and physicists as well:

i) Bond Length and Angle Variations, Strain

The present knowledge of the properties of the pure AlO_4 tetrahedron is surprisingly restricted. This is due, on the one hand, to the relatively small number of aluminate structures which have been determined with sufficient precision, and, on the other hand, a result of the fact that in aluminosilicates the behaviour of the AlO_4 tetrahedron is masked by that of the SiO_4 tetrahedron [4]. Thus, aluminate sodalites offer a good opportunity to study the Al-O bond and the Al-O-Al angle in their pure form and provide the theoretical chemist with empirical data to test his calculations (cf. ref. 4). Furthermore, the repulsive interactions produce strong local angular and also bond length distortions within the framework, whereby the interactions and corresponding distortions depend on the temperature (phase transitions, see below). Therefore, as structural work advances, a growing wealth of information on the pure AlO_4 tetrahedron should come to our disposal. The

study of the effects of intrinsic and extrinsic strains in the relatively simple sodalite structure should also facilitate studies in the more complicated zeolites, where these effects recently also began to attract attention (see, e.g. ref. 5).

(ii) Phase Transitions

The distortion of the framework means, in general, that the symmetry is lowered. The deviation from cubic symmetry can, however, be cancelled by order-disorder processes which might be brought about by either raising the temperature or by changing the composition of mixed crystals. All pure aluminate sodalites known so far are non-cubic at room temperature and undergo structural transitions at temperatures which range between ~300 K and ~700 K. The phase transitions are of the ferroic type; ferroelastic and ferroelectric species have been found so far [6]. The transitions occur at the boundary of the Brillouin zone; this fact accounts for the formation of complicated superstructures and for frequent pseudomerohedral twinning. First steps towards a phenomenological theory have been done; however, there are still many points which remain unclear; e.g., it is still a matter of question whether there is only one theory for all aluminate sodalites or more than one according to the various degrees of host - guest interaction. Very intriguing results come from studies on mixed crystals [7] which indicate the existence of tricritical points. Their study would be interesting in view of the six-component order parameter and because of possible implications for current theories of phase transitions [8].

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