Hyperfine interactions between unpaired electrons and framework atoms in aluminosilicate sodalites containing paramagnetic Na_4^{3+} clusters: a ^{29}Si and ^{27}Al MAS NMR study

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First NMR evidence is presented for hyperfine interactions between unpaired electrons and the framework atoms in alkali-metal doped zeolites by the ^{27}Al and ^{29}Si MAS NMR spectra of aluminosilicate sodalites loaded with paramagnetic Na_4^{3+} clusters which show up to seven resonances with characteristic down-field shifts caused by Fermi contact interactions between the unpaired electrons of the sodium clusters and the Al and Si atoms of the sodalite framework.

Sodium aluminosilicate sodalites are characterized by a microporous framework composed of a perfectly periodic array of all-space filling $[4^6 6^8]$ polyhedra (also called sodalite cages or β-cages), which are formed by an alternating network of corner-sharing SiO_4 and AlO_4 tetrahedra. Besides the three sodium cations compensating the negative framework charge, the cages may accommodate water molecules and/or additional cations and anions, yielding a general unit-cell composition of $[Na_{6+x}A_x(H_2O)_n][Si_6Al_6O_{24}]$, where A is a univalent anion and $0 \leqslant x \leqslant 2$.[1] When anhydrous sodalite of composition $Na_6[Si_6Al_6O_{24}]$ is exposed to sodium vapour, each sodalite cage can absorb an additional sodium atom which is spontaneously ionized and shares its electron with the three charge-compensating Na^+ ions in the cage, forming a paramagnetic $(Na^+)_4e^- \equiv Na_4^{3+}$ cluster.[2] The formation and tetrahedral geometry of the cluster within the sodalite cage is schematically depicted in Fig. 1. Depending on the concentration of absorbed sodium in the sodalite, its colour changes from white to blue, purple and finally to black. Therefore, the designation 'black sodalite' is adopted for highly sodium-loaded samples. Formation of paramagnetic alkali-metal clusters of various types has also been observed for other zeolites and a variety of alkali metals.[3] Materials of this kind are of high interest due to their structural, optical, electronic and magnetic properties, and a number of theoretical and experimental studies are devoted to this subject in the recent literature (see ref. 4 and references therein). In this communication, the first application of solid-state ^{27}Al and ^{29}Si NMR spectroscopy to sodium-loaded black sodalites is presented which provided detailed information on the interaction between the unpaired electron in the sodium cluster and the sodalite framework.

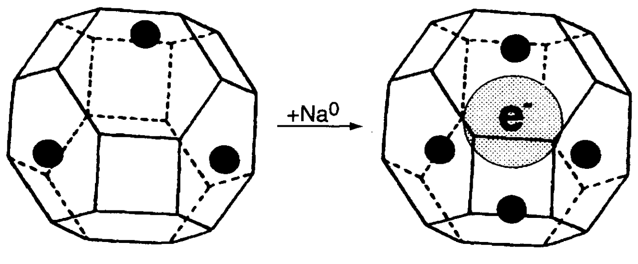

Fig. 1 Sodalite cages containing diamagnetic Na_3^{3+} (left cage) and paramagnetic Na_4^{3+} clusters (right cage). Alternating Si and Al atoms at the vertices of the cage structure are interconnected by oxygen atoms which are omitted for clarity. Black circles represent Na^+ cations located above the centres of the six-rings.

Sodium-loaded black sodalites {ideal composition at full loading $Na_8[Si_6Al_6O_{24}]$} were prepared from dehydrated non-basic sodium sodalite, $Na_6[Si_6Al_6O_{24}]$, by treatment with sodium metal vapour under vacuum at elevated temperature.[2,5] The structural integrity of the loaded samples was established by X-ray diffraction. ^{27}Al and ^{29}Si MAS NMR spectra of the samples were measured at 104.26 and 79.49 MHz, respectively, using a Bruker MSL-400 spectrometer equipped with standard MAS probes for 4 mm (^{27}Al) or 7 mm (^{29}Si) rotors. The samples were filled into the MAS rotors in a glove box under dry nitrogen gas.

Fig. 2 displays the ^{29}Si and ^{27}Al MAS NMR spectra of a typical black sodalite sample. In contrast to the unloaded anhydrous sodalite which shows single lines of the framework Si and Al atoms in the ^{29}Si NMR (δ −90.5) and ^{27}Al NMR spectra (δ 52.3), seven resonances (labelled 1–7 in Fig. 2) can be identified in the corresponding spectra of black sodalite which are shifted to low field by up to 70 ppm (line 7). Lines in this range have never been observed before for SiO_4 or AlO_4 environments in any aluminosilicate and are caused by paramagnetic shifts due to interaction of the ^{29}Si and ^{27}Al nuclei

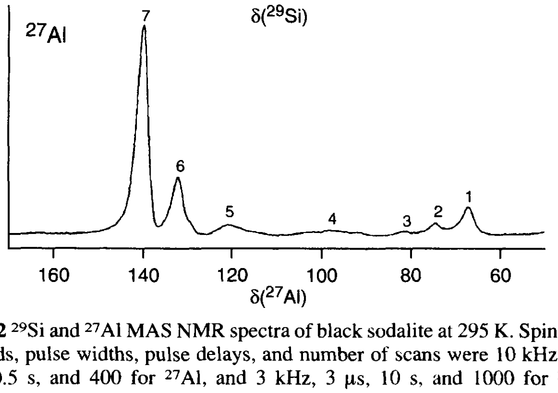

Fig. 2 ^{29}Si and ^{27}Al MAS NMR spectra of black sodalite at 295 K. Spinning speeds, pulse widths, pulse delays, and number of scans were 10 kHz, 0.7 μs, 0.5 s, and 400 for ^{27}Al, and 3 kHz, 3 μs, 10 s, and 1000 for ^{29}Si, respectively. * Denotes spinning side bands.

with the unpaired electrons associated with the Na_4^{3+} clusters. The size of the paramagnetic shift, $\Delta\delta$, depends on the number of cages containing paramagnetic Na_4^{3+} (hereafter designated A-cages) and diamagnetic Na_3^{3+} units (B-cages) surrounding the respective T atom (T = Si, Al). Since each T atom is part of four cages, lines 7, 6, 5, 4 and 1 (see Fig. 2) are attributed to [nA(4 − n)B] environments with n = 4–0, respectively, while lines 2 and 3 are assumed to originate from [0A4B] environments with one or two second nearest A-cages. As to be expected for paramagnetic shifts, variable-temperature ^{27}Al MAS NMR measurements reveal a considerable temperature dependence of the line positions which follows the Curie–Weiss law and decreases from line 7 to line 2 but vanishes for line 1. These results will be discussed in more detail in a forthcoming paper. The above line assignment is further corroborated by the characteristic changes in the line intensities of the ^{29}Si and ^{27}Al NMR spectra observed for sodium-loaded sodalite samples prepared from sodium bromide sodalites, $[Na_{6+x}Br_x][Si_6Al_6O_{24}]$, with $0 < x < 2$.[6] In these structures, some of the cages are occupied by NaBr, and thus not accessible to the formation of Na_4^{3+} clusters.

From the relative integrated line intensities, I_n, the percentage of A-cages, *i.e.* the degree of sodium loading, can be estimated according to %A = $100\Sigma I_n/\Sigma(0.25nI_n)$, which yields 73% for the particular sample shown in Fig. 2. Black sodalites with higher Na_4^{3+} loadings have also been prepared, their ^{29}Si and ^{27}Al NMR spectra show mainly line 7 and exhibit only very weak intensities of the other lines.

In principle, there are two origins of paramagnetic shifts caused by unpaired electrons: (*i*) the Fermi contact shift which arises from the isotropic interaction of the nuclear spin with the net electron spin density at the nucleus, and (*ii*) the pseudo-contact shift due to anisotropic dipolar interaction of the electron spin and the nuclear spin. There are strong arguments (*e.g.* isotropic electron g factors from EPR,[7] only weak spinning side bands in the MAS NMR spectra, line position not affected by sample rotation,[8] temperature-independent linewidths[9]) to conclude that in the black sodalites the Fermi contact shift predominates. The latter is given by[10] $\Delta\delta = -A_N(\gamma_e/\gamma_N)hS(S+1)10^6/3kT$, where A_N is the Fermi contact coupling constant which is usually observed from hyperfine splittings in EPR experiments. However, hyperfine splitting with the framework Al or Si atoms in black sodalites is too small to be detectable in the EPR (or ESEM) spectra.[7] It seems, therefore, important that A_N can now be easily calculated from the paramagnetic NMR shifts $\Delta\delta$ (in ppm) by the relation $A_N = 0.141\Delta\delta\gamma_N 10^{-3}$ which follows from the above equation with $T = 300$ K and $S = 1/2$. A_N values in the range of about 60–700 kHz were obtained from $\Delta\delta$ observed for the various resonance lines in the spectra of Fig. 2. Moreover, since A_N is related to the density of the unpaired electron at the interacting nucleus,[10] $|\Psi(0)|^2$, by $A_N = (8\pi/3)g_e\mu_B\gamma_N|\Psi(0)|^2$, the latter quantity can also be determined from the NMR spectra and amounts to about 6.3×10^{-4} to 2.7×10^{-4} a.u. for T atoms in the [nA(4 − n)B] environments with n = 4–1, respectively, with slightly but invariably lower values for Si than for Al.

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