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High Field ^{27}Al ENDOR Reveals the Coordination Mode of Cu^{2+} in Low Si/Al Zeolites

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Copper exchanged zeolites have been of interest since the late 1970s due to their catalytic properties.[1] This stimulated investigations of the location and coordination shell of the Cu ions within the zeolite structure which can account for the catalytic activity. Spectroscopic methods, particularly EPR spectroscopy and electronic spectroscopy, have been used extensively to provide information on the oxidation state, the identity, and the quantity of the Cu^{2+} centers in low level Cu-exchanged zeolites.[2−5] The various Cu^{2+} species are usually identified by their distinct $g_{\|}$ and $A_{\|}$ EPR parameters, and for a particular zeolite several species often coexist, depending on the hydration state and the Si/Al ratio. The EPR parameters have been traditionally interpreted based on the well-established distinct cation sites within the zeolite structure.[2,3] Although numerous studies have been reported, the interpretation of the experimental results in terms of specific locations (siting) is still being debated.

Additional new insights into the issue of Cu^{2+} siting in zeolites have been recently provided by ab initio calculations.[4,6−8] Such calculations, first carried out on cluster models of structures with a large Al content, aimed at reproducing the experimental g-values and optical spectra of Cu^{2+} in dehydrated zeolites A, ZK-4, X, and Y.[6] An interesting outcome of these calculations was that the Cu^{2+}, which prefers site II (center of the six-member ring, 6MR), adapts a tetragonal coordination sphere by coordinating four zeolite oxygens, and not a trigonal geometry, as believed earlier. This, in turn, inflicts a considerable distortion to the 6MR. Moreover, the study showed that the differences in g-values could arise also from different numbers of Al in a 6MR and not only from different site topology, as believed earlier. Other Density Functional Theory (DFT) calculations have shown that the spin density is distributed both on the Cu and on framework oxygens and that the Cu anisotropic hyperfine interaction was closely related to the Cu−O distance and coordination number.[8] These assignments and predictions can, in principle, be verified experimentally by examining the NMR frequencies of framework ^{27}Al coupled to the Cu^{2+}. This should yield both the ^{27}Al hyperfine and quadrupole interactions that in turn provide the geometry of the site and the degree of framework distortion induced by the Cu^{2+} binding. Such attempts have been carried out using ^{27}Al electron spin−echo envelope modulation (ESEEM) spectroscopy.[9,10] Indeed, these experiments revealed a finite ^{27}Al hyperfine coupling of $\sim$2−3 MHz in zeolite X and A, showing clear evidence for Cu^{2+} binding to zeolite oxygens next to an ^{27}Al. Furthermore, sitting in the six-member ring was deduced from orientation dependence of the modulation depth.[10] Later, a two-dimensional variant of ESEEM, hyperfine sublevel correlation (HYSCORE) spectroscopy was applied to study dehydrated Cu^{2+} in zeolite Y (Si/Al = 12).[11] The spectrum clearly showed the presence of ^{27}Al hyperfine couplings. Although the spectrum was rich, its interpretation was complex and the hyperfine and quadrupole parameters could not be determined uniquely. Here we present high field (W-band, 95 GHz/3T) electron−nuclear double resonance (ENDOR) results which finally provided highly resolved ^{27}Al ENDOR spectra of Cu^{2+} in zeolite X (Faujasite structure with Si/Al = 1). This was possible because of the higher nuclear Larmor frequency, which is most important for low γ nuclei, such as ^{27}Al, ^{13}C and ^{17}O, and the better orientation selection. These measurements yielded both the ^{27}Al hyperfine and quadrupole tensors, showing that indeed the Cu^{2+} is situated in the 6MR and the three Cu−Al distances are equal.

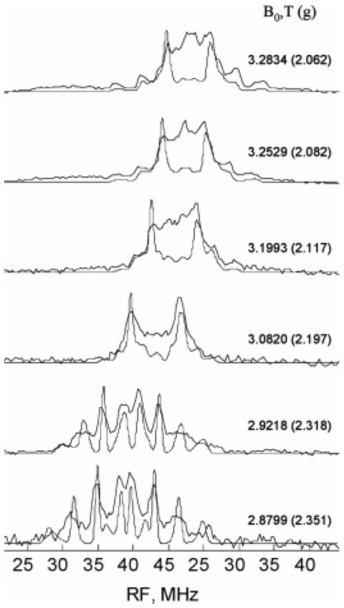

Figure 1. Orientation selective W-band Davies ^{27}Al ENDOR spectra (black lines) of D-Cu-FAU-1.0 recorded at the indicated field positions and g-values (in parentheses), along with simulations (gray lines) obtained using EasySpin[14] with the parameters listed in Table 1. Experimental parameters: microwave pulse length 0.20, 0.10, and 0.20 μs, respectively, τ = 0.40 μs, RF pulse length 15.0 μs, temperature 5 K.

The parent X zeolite (NaFAU Si/Al = 1) was prepared according to the method of Melchior et al.[12] Cu^{2+} was exchanged as described earlier.[9] If all of the Cu^{2+} in solution exchanged into the zeolite, the Cu/unit cell (UC) in the sample would be 0.4. The dehydration procedure is given in the Supporting Information, and the dehydrated sample is referred to as D-Cu-FAU-1.0. The X-band and W-band EPR spectra show the presence of a single Cu^{2+} type with $g_{\perp} = 2.06$, $g_{\|} = 2.38$, and $A_{\|} = 410$ MHz, which agree well with the literature values.[13,4]

A series of orientation selective W-band Davies ENDOR spectra of D-Cu-FAU-1.0 are shown in Figure 1. The spectrum recorded closest to $g_{\|}$ (2.8799 T) is single crystal like and therefore it is

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Table 1. Best Fit ^{27}Al a_{iso}, Anisotropic Hyperfine Components, T_{xx}, T_{yy}, T_{zz}, Quadrupole Coupling Constant, e^2qQ/h (in MHz), Asymmetry Parameter, η, and the Orientation of the Hyperfine and Quadrupole Tensors Relative to the *g*-Tensor Principal Axis System

a_{iso}	T_{xx}, T_{yy}, T_{zz}	α,β,γ	e^2qQ/h	η	α',β',γ'
−3.43	−0.66,−0.07,0.73	$0,90,0^0$	14.8	0.7	$90,90,0^0$

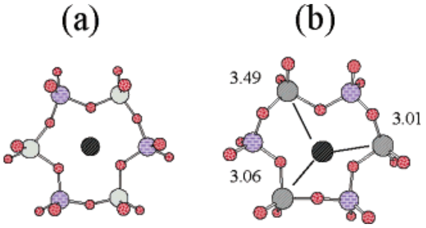

Figure 2. (a) Position of the Cu^{2+} in the center of an undistorted 6MR and (b) in structure E obtained by Pierloot et al.[6] The numbers give the Cu−Al distance in Å.

highly resolved, showing a superposition of two equivalent quintets, with a splitting of ∼1.6 MHz. This splitting is due to the quadrupolar splitting of the ^{27}Al nucleus ($I = {}^5/_2$). The distance between the centers of the two quintets yields a hyperfine coupling of 4.2 MHz. As the field increases toward $g_\perp$ the lines broaden and the splittings change, revealing a clear orientation dependence due to the large spread of the *g*-anisotropy which at W-band exceeds the copper hyperfine anisotropy. The whole set of orientation selective ENDOR spectra could be well reproduced by simulations using one type of ^{27}Al nucleus with the hyperfine and quadrupolar parameters listed in Table 1. Here a negative value was assigned to the isotropic hyperfine constant, a_{iso}, to allow for a positive anisotropic hyperfine component, T_{ZZ}. The orientation of the tensor relative to the g tensor principal frame, given by α,β,γ, shows that the ^{27}Al is situated in a plane perpendicular to $g_{||}$. Only a highly symmetric geometry of Cu^{2+} in the 6MR with three equal Cu−Al distances, in a trigonal symmetry, and $g_{||}$ perpendicular to the Cu−Al axis could be described by a single ^{27}Al with the parameters listed in Table 1. An example of such a site is shown in Figure 2a, where the Cu^{2+} is coordinated to only three oxygen atoms. This is similar to the siting of Mn^{2+} in fully exchanged Mn−X zeolite determined by single-crystal X-ray diffraction analysis.[15]

In their theoretical work Pierloot et al.[6] considered Cu^{2+} coordinated to six different cluster model structures of the six-member ring appearing in zeolites A and Y (or X) that are distinguished based on the number and positions of Al in the 6MRs (see Figure S1). The ring structures were obtained from structure optimization of cluster models. Out of these, structure E, corresponding to three Al in a 6MR, shown in Figure 2b, is relevant to D-Cu-FAU-1.0. It has two different Cu−Al distances and therefore two ^{27}Al signals are expected. Using the coordinates of these optimized structures, DFT calculations were carried out using the program ORCA[16] (see Supporting Information for more details) and the ^{27}Al hyperfine tensors for each of the model clusters was obtained (see Table S1). Structure E indeed gave one Al with $a_{\mathrm{iso}} = -3.8$ MHz and the other two with $a_{\mathrm{iso}} = -1.5, -1.2$ MHz. The experimental results, however, show that all Al are equivalent, and therefore structure E does not describe satisfactorily the 6MR for Si/Al = 1. The experimental a_{iso} value, −3.43 MHz, is close to that of the more strongly coupled ^{27}Al. The calculated anisotropic principal components (−1.6, −0.44, 2.04) are overestimated, but the relatively large deviation from axial symmetry is reproduced. This is attributed to a significant spin density on the oxygen. The calculations yielded Loedwin spin densities in the range 0.05−0.11 for four of the oxygens. The experimental results do not exclude the possibility that the Cu^{2+} is still coordinated to four oxygens, but the structure must allow equal Cu−Al distances. This would require displacement of the Cu^{2+} along with a change in the conformation of the ring.

The quadrupole coupling constant found is rather large, 14.8 MHz, compared to ^{27}Al in other dehydrated zeolites determined by NMR. These are 4−6 MHz in NaY and NaZSM-5[15] and 10−16 MHz in HX, HY, and HZSM-5.[17,18] It shows that the distortions induced on the Al tetrahedra by the Cu^{2+} binding to the zeolite oxygens are considerably higher than those for Na$^+$. The experimental results provide also the direction of the quadrupole interaction, which usually cannot be obtained from NMR measurements on powders. The direction of Q_{zz} was found to be in the plane perpendicular to $g_{||}$, perpendicular to the T_{zz} direction, which is close to the Cu−Al directions.

To conclude, we have shown that high field ^{27}Al ENDOR gave a detailed picture of the spatial and electronic structure of the Cu^{2+} sites in dehydrated zeolite X. The tensors determined can now provide additional valuable constraints for DFT calculations, which can model the structure of the site in detail. Naturally, this can be extended to other zeolites and other paramagnetic metal ions.

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Supporting Information Available: Details of sample dehydration procedure and of DFT calculation method. Structures of the cluster models obtained by Pierloot el al[6] of Cu^{2+} coordinated to six different six-member ring structures appearing in zeolite A and Y. A Table of the DFT calculated ^{27}Al hyperfine couplings of the structure shown in Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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