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Communications to the Editor

Complexation of Copper by Cyclohexadienyl Radicals in Cu/ZSM-5 Zeolite

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We report the first observation of a complex of a neutral organic free radical with a diamagnetic metal ion in a zeolite, specifically of the cyclohexadienyl radical with copper in Cu/ZSM-5, an important catalyst for NO decomposition. The results give evidence of the location of the copper in the zeolite, and of a relatively weak perturbation of the organic radical in the complex.

It is well-known from NMR experiments that benzene in faujasites interacts with its π-system with sodium cations of known location in the supercage, thereby retaining a high rotational mobility about its 6-fold axis.[1] Due to their open shell nature, chemical interactions of radicals are in general expected to differ from those of comparable diamagnetic molecules. Paramagnetic transition metal ions and their interactions with small diamagnetic molecules were studied with use of ESR.[2] The reverse case, i.e., the interaction of organic radicals with diamagnetic ions, has not yet been observed in zeolites.

The present observations are based on a variant of magnetic resonance which in short is as follows:[3] The sample is irradiated with positive muons, which are spin-$^{1}/_{2}$ elementary particles with a magnetic moment 3.18 times that of the proton, a lifetime of 2.2 μs, and a mass of one-ninth the proton mass. Near the end of its thermalization track, the muon captures an electron, thereby forming a bound state, called muonium (Mu), which is in a chemical sense a light isotope of hydrogen. Mu reacts with unsaturated molecules by addition, placing the polarized muon spin label in a radical. The experimental technique takes advantage of avoided crossings of magnetic energy levels in an external magnetic field, thereby leading to resonances in a plot of the integral muon polarization as a function of the field. The positions of the resonances of selection rules Δ_1 and Δ_0 are related to the hyperfine coupling constants of the radical.[3]

Samples were prepared with zeolites provided by CU Chemie Uetikon in Switzerland. NaZSM-5 with a Si/Al ratio of 900, which below we will call silicalite, was calcined at 720 K. HZSM-5 with Si/Al = 50 was calcined at 770 K, exchanged three times with 0.5 M aqueous $Cu(NO_3)_2$ at 350 K, washed three times, and then dried under vacuum at 450 K. This treatment results in at least partial reduction to Cu^+,[2] or in an excessively exchanged Cu/ZSM-5 with mostly EPR-silent copper species which were assigned to $[Cu{-}O{-}Cu]^{2+}$ complexes.[4] Since the two diamagnetic copper species will be difficult to distinguish in our experiment we will term it Cu^+ in the following. Both samples were placed in stainless steel cells with a window of 25 μm thickness, loaded with 2.3 wt % of benzene, and sealed. Experiments were carried out at the πE3 beam port of the cyclotron at the Paul Scherrer Institute in Switzerland which provides muons with a spin polarization close to 100%.

Table 1. Hyperfine Coupling Constants (MHz) and Electron Spin Population on the Cation

	C_6H_6Mu/ silicalite	$Cu\cdots C_6H_6Mu$/ ZSM-5	$Ag\cdots C_6H_7$[a]
$A_\mu\,\mu_p/\mu_\mu$	158.7	159.9	
A_n(methylene-H)	124.0	125.5	126.7
A_n(*o*-H)	−25.7	n.o.[b]	−24.9
A_n(*m*-H)	n.o.[b]	n.o.[b]	7.3
A_n(*p*-H)	−36.7	n.o.[b]	−36.4
A_n(cation)		161.0	51.8
ρ_s(cation)		2.7%	2.8%

[a] Gee and Wan, ref 10. [b] Not observed.

The figure displays the spectrum obtained upon muon irradiation of benzene in ZSM-5 type structures at a loading of two molecules per unit cell, corresponding to ca. 25% of the maximum sorption capacity. The top line shows two sharp features in silicalite which are assigned to the Δ_1-resonance and to the methylene proton Δ_0-resonance of the muonated cyclohexadienyl radical, C_6H_6Mu, in accord with the known coupling constants of the species.[5] Two weaker Δ_0-resonances related to the ortho and para protons were observed at fields of 2.8745 and 2.9546 T, whereas the meta proton line remained undetected because of its low intensity. The sharpness of the lines indicates extensive averaging of the hyperfine anisotropy by large amplitude fast reorientational motion.[6] This high mobility shows that the benzene molecules from which the radicals are derived must be located at the channel intersections, a finding that has been derived also from molecular dynamics calculations.[7] The mere presence of the Δ_1-resonance proves a residual anisotropy of the dynamics.[6]

The second spectrum was obtained with copper exchanged ZSM-5. The same two resonances as in the silicalite are clearly present, although significantly broadened. Obviously, there is considerably less motional averaging. The two higher field resonances were too broad to be detected, and instead there is a dominant additional band at 1.389 T. Since the latter is not expected for the isolated radical it can only be due to hyperfine interaction with a diamagnetic copper nucleus, i.e., with Cu^+. It is broadened by unresolved splitting due to the two copper isotopes (^{63}Cu, $I = {}^{3}/_{2}$, 69%; ^{65}Cu, $I = {}^{3}/_{2}$, 31%) and to the nuclear quadrupole moments. Similar results were obtained in preliminary experiments with LiZSM-5, where the $\Delta_0(Li^+)$ resonance shifted to ca. 1.72 T, and with NaZSM-5 where the $\Delta_0(Na^+)$ line is observed at 1.69 T.[8] In all cases where metal cations are present the lines narrow considerably when the temperature is raised above 300 K, which indicates that the complexed species is also not rigidly fixed to the zeolite lattice. The absence of narrow components in the resonances of the ionic systems shows that all benzene molecules are coordinated, whereas previous experiments at higher benzene loadings gave evidence of two-component signals.[9] Monovalent Cu^+ thus appears to be more mobile and

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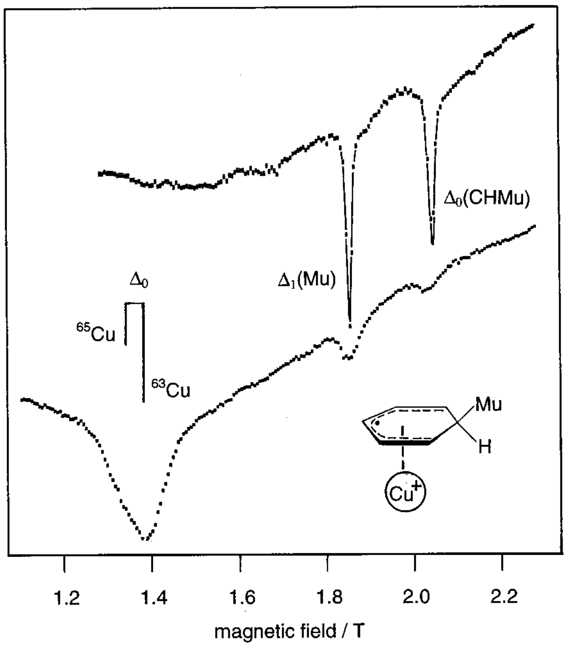

Figure 1. Avoided level crossing muon spin resonance spectra obtained with benzene in silicalite at 361 K (upper trace) and in Cu/ZSM-5 at 433 K (lower trace). The resonances are assigned to the free and to the Cu-complexed Mu-substituted cyclohexadienyl radical.

more readily available for complexation than Cu^{2+}, which was found to be quite inaccessible to benzene and to other nonpolar molecules.[2]

The hyperfine coupling constants derived from the spectra are given in Table 1, together with literature values for the interactions of the same radical complexed with Ag^+ in polycrystalline cyclohexadiene.[10] All coupling constants are surprisingly similar for the different systems, indicating that the radical structure is affected very little by the interaction with the cation. The reduced methylene muon couplings are higher by 28% than the corresponding proton couplings owing to the slightly longer bond of the lighter nucleus in the anharmonic potential.[11] The copper cation coupling amounts to 161 MHz. We calculate the s-orbital spin population, ρ_s, on the basis of the experimental coupling of 5995 MHz [12] for the ^{63}Cu atom. It is strikingly similar for Cu^+ and for Ag^+ (which are in the same group of the periodic table) despite the entirely different environment, and amounts to less than 3%, demonstrating again the relatively weak interaction. As for the benzene[1] and cyclohexadiene[10] parent molecules we assume that the cation coordinates with the ligand via the electrons of the polarizable π-system.

By crystallographic methods it has not been possible so far to locate the cations in ZSM-5 type zeolites, possibly because there are no unique cation sites. The present results demonstrate that cation and radical find each other within a distance over which limited chemical interaction is possible. Since the residual dynamics indicates that the cyclohexadienyl radicals still sit at the channel intersections this means that in the presence of the organic molecule the cations migrate to the intersections, or they were there already before the organic was introduced.

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