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An Electron Paramagnetic Resonance Study of Mono-(2,2'-bipyridine)copper(II) Complexes Formed in Zeolite-Y

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Transition metal complexes may be formed in zeolites by a variety of techniques including exchange of the hydrated ion followed by dehydration and addition of the ligand from the gas phase [1], direct exchange of the complex ion [2], and exchange of the ligand followed by the addition of the metal ion [3]. By employing the latter technique with protonated tetraethylenepentamine as the ligand it has been demonstrated in clay minerals that complexing ions such as Ni^{2+} and Cu^{2+} may be very efficiently removed from aqueous solutions.

In the present work we describe the formation of mono(2,2'-bipyridine)copper(II) complexes in zeolite Y. This work is part of a larger program directed toward the photochemistry of transition metal complexes in zeolites. Since copper(II) ions can be easily detected by epr spectroscopy, they serve as a good model for studying complex formation with bipyridine in zeolites. The epr data indicate that during complex formation a proton on the exchanged bipyridinium ion is replaced by copper, and a chelate complex is formed with the metal ion.

The bipyridinium form of the zeolite was prepared by exchanging a NaY zeolite (Union Carbide) with 2,2'-bipyridinium chloride (K & K Laboratories). For the exchange 5g of the zeolite was brought into suspension in 3.5 l H_2O. Bipyridinium chloride was added to this suspension while monitoring the pH to make sure it did not fall below 3.5. The addition of bipyridine was stopped when the pH remained constant over a period of 2h. The zeolite was then filtered, washed with water until free of chloride ions, and dried at 25 °C. The bipyridine concentration was determined by dissolving the zeolite in citric acid and determining the absorbance at 295 nm. The bipyridine concentration was found to be 1.1 molecules/unit cell or 0.14 molecules/large cavity.

This bipyridinium zeolite was subsequently exchanged with $^{63}Cu^{2+}$ ions in a solution of $^{63}Cu(NO_3)_2$ to a level of 0.5% of the total cation exchange capacity. This corresponds to 0.14 ions/unit cell or 0.02 ions/large cavity. The zeolite was again filtered from solution, washed and dried at 25 °C.

The epr measurements were carried out at 77 K using a Varian E-6S spectrometer. The g values were determined relative to a DPPH standard. The spectrum was simulated with the program SIM 13, [4] assuming axial symmetry.

After degassing the sample slowly to 150 °C the epr spectra shown in curves a and b of Fig. 1 were obtained. Upon treatment of the sample with O_2 at 150 °C and subsequent evacuation at 25 °C the intensity of the spectrum increased but the shape remained the same, indicating a reoxidation of some copper ions which underwent reduction during degassing.

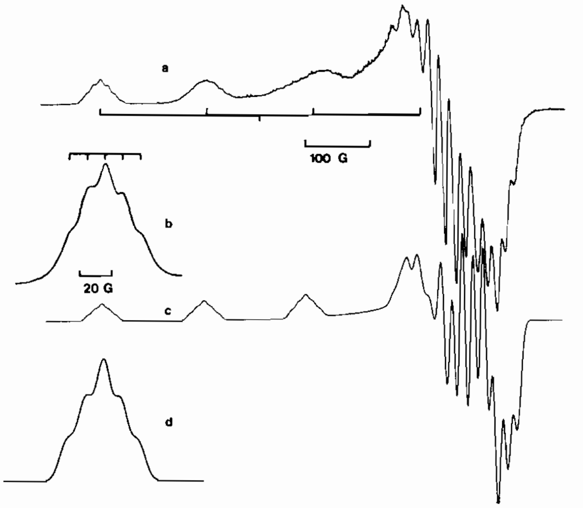

Fig. 1. Epr spectra of $[Cu^{II}(bipy)]^{2+}$ in zeolite-Y: (a) experimental curve, (b) ^{63}Cu, $m_I = -3/2$ region, expanded scale, (c) simulated spectrum, (d) ^{63}Cu, $m_I = -3/2$ region, expanded scale.

The positions of the lines in the experimental spectra are reproduced by the simulated spectra of curves c and d; however, the relative intensities of several lines in the high field region differ somewhat. Nevertheless, the overall agreement obtained with the following parameters is reasonably good: $g_\parallel = 2.263$, $g_\perp = 2.037$, $A_\parallel^{63Cu} = 0.0166\ cm^{-1}$, $A_\perp^{63Cu} = 0.0026\ cm^{-1}$, $A_\parallel^N = 0.0012\ cm^{-1}$ and $A_\perp^N = 0.0015\ cm^{-1}$.

The most important feature of the spectrum is the five-line superhyperfine structure which is resolved for the ^{63}Cu, $m_I = -3/2$ component. This superhyperfine structure provides evidence that the copper(II) ion is bonded to two equivalent nitrogen atoms (I = 1). Thus, we attribute the spectrum to $[Cu^{II}(bipy)]^{2+}$, in which the copper may also be bonded to oxide ions of the zeolite lattice, or to a water molecule since the zeolite was not totally dehydrated. The observation of the superfine structure in the zeolite is essential for the identification of the complex since both mono- and tris-complexes formed in ethanol-water solutions have values of $g_{\parallel}$ and $A_{\parallel}^{Cu}$ which are similar to those reported here [5]. For example, the complex $[Cu^{II}(bipy)(H_2O)_4]^{2+}$ has $g_{\parallel} = 2.305$ and $A_{\parallel}^{Cu} = 0.0164$ cm^{-1} while $[Cu^{II}(bipy)_3]^{2+}$ has $g_{\parallel} = 2.260$ and $A_{\parallel}^{Cu} = 0.0165$ cm^{-1}. In the presence of borate buffers $A_{\parallel}^{Cu}$ increased to 0.0174 cm^{-1} for the mono-complex.

It is also interesting to compare the magnetic parameters observed here with those previously reported for another chelating agent, ethylenediamine [2]. For the mono(ethylenediamine)copper(II) complex in hydrated zeolite-X the parameters were $g_{\parallel} = 2.268$, $g_{\perp} = 2.053$, $A_{\parallel}^{Cu} = 0.0175$ cm^{-1} and $A_{\perp}^{Cu} = 0.0013$ cm^{-1}. These values are similar to those reported here for the bipyridine complex, but, the agreement may be somewhat fortuitous since dehydration of the zeolite-X at 25 °C caused modifications in the spectrum (*e.g.* $g_{\perp} = 2.239$ and $A_{\parallel}^{Cu} = 0.0181$ cm^{-1}).

Although it was not confirmed by infrared spectroscopy, one would assume that the bipyridinium ion was present in the zeolite prior to the introduction of Cu^{2+}. In the process of coordination the copper ions must selectively replace the protons from the nitrogen; however, the protons undoubtedly continue their function as exchange cations. Under the conditions of this study all of the Cu^{2+} ions became coordinated to the bipyridine; *i.e.*, none was coordinated only to the oxide ions of the zeolite. These observations may be important in understanding the mechanism for the selective removal of trace amounts of Cu^{2+} from solution by ion exchange into clays which contain chelating cations.

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