Zeolite-Encapsulated Copper(II) Amino Acid Complexes: Synthesis, Spectroscopy, and Catalysis

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The spectroscopic properties and catalytic behavior of $Cu(AA)_n^{m+}$ complexes (AA = amino acid (glycine, lysine, histidine, alanine, serine, proline, tyrosine, phenylalanine, glutamine, glutamic acid, cysteine, tryptophan, leucine, and arginine)) in faujasite-type zeolites have been investigated. Successful immobilization was achieved by a simple cation exchange procedure with aqueous solutions of preformed $Cu(AA)_n^{m+}$ complexes. The best ion exchange results were obtained with lysine, arginine, proline (at pH = 10), and histidine (at pH = 7.3) as ligands and with a AA:Cu^{2+} ratio of 5. The internal surface and pore volume are drastically reduced by the uptake of the $Cu(AA)_n^{m+}$ complexes, and no precipitation of $Cu(AA)_n^{m+}$ crystals was observed by scanning electron microscopy. Both observations suggest the location of the complexes in the supercages of the faujasite-type zeolites. The composition of the first coordination sphere around Cu^{2+} can be designed from NNNN to NOOO by varying the type of amino acid. A free coordination site is available for catalysis, and the oxidation of alcohols, alkanes, and alkenes with peroxides was observed at low temperatures.

Introduction

$Cu(AA)_n$ complexes (AA = amino acid) have already been the subject of detailed investigations in solution. Complexation constants of different AA with Cu^{2+} were determined.[1,2] The type of binding between an AA and Cu^{2+} is the same for all α-amino acids with the exception of histidine.[3,4] The general coordination for a Cu complex with two α-amino acids is the binding of both AA by an amino nitrogen and a carboxyl oxygen, i.e., a NNOO coordination or a glycine-like bonding. For $Cu(histidine)_2$ in the pH region 4.5−7.5, the two histidine ligands are coordinated to Cu^{2+} in the coordination plane by the amino N and the imidazole N, while the carboxylate group coordinates in an apical position. However, the carboxylate oxygen of one of the histidine ligands can replace partially one of the imidazole nitrogens and an equilibrium exists between NNNN and NNNO bonding in the coordination plane of bis-(histidine) complexes.[4] NNNN coordinations are called histamine-like bonds, and in NNNO species one histidine is bound histamine-like and the other glycine-like.

$Cu(AA)_n$ complexes represent mimics of the active center of natural Cu enzymes, which are known to be the most abundant, active, and selective catalysts in nature for oxidation reactions.[5−7] The operational domain of enzymes is, however, relatively narrow as far as temperature and solvent are concerned. Enzyme mimicking is the building of the active center of enzymes into an inorganic matrix, which allows a larger operational temperature domain in a broader spectrum of solvents.[8,9] The inorganic matrix can be a zeolite structure in which the complex is immobilized and a heterogeneous system can be developed.

Here, we report on a simple ion exchange procedure for the immobilization of $Cu(AA)_n^{m+}$ complexes into zeolite Y, as was briefly announced for Cu(histidine) complexes in a recent note.[10] Three subjects will be studied systematically: (1) the ion exchange of preformed $Cu(AA)_n^{m+}$ complexes in zeolites, (2) the spectroscopic fingerprinting of immobilized $Cu(AA)_n$ complexes, and (3) the catalytic behavior of immobilized $Cu(AA)_n^{m+}$ complexes. These data allow a detailed discussion of the coordination chemistry of zeolitic $Cu(AA)_n^{m+}$ complexes.

Experimental Section

1. Sample Preparation and Treatments. NaY from Ventron (with a Si:Al ratio of 2.49 and a cation exchange capacity of 4.32 mequiv/g) was put in the Na^+ form by two successive exchanges with 1 M NaCl solutions, washed Cl^--free and dried in air at room temperature overnight. A 2.5 g quantity of NaY was stirred in a $Cu(AA)_n$ solution of 500 mL distilled water containing 1.33×10^{-3} M $Cu^{II}(NO_3)_2 \cdot 3H_2O$ (Merck) (±4 Cu/UC NaY) and 6.67×10^{-3} M AA. The amino acids from Janssen Chimica are L-alanine (99%), L-(+)-arginine (98%), L-(+)-cysteine, L-(+)-glutamine (99%), glycine (p.a.), L-histidine (98%), L-(+)-lysine hydrate (99%), D-phenylalanine (99%), and L-(−)-tryptophan (99%). The amino acids from Merck are L-leucine, L-(−)-proline, L-(−)-serine, L-(−)-tyrosine and from Borgers glutamic acid (99%). The $Cu(AA)_n$ solution was brought to a specific pH by using either a NaOH or HCl solution. After ion exchange, the samples were separated from the solution by centrifugation, washed, and dried at 60 °C overnight in air.

2. Characterization Methods. Electron spin resonance (ESR) spectra were recorded on a Bruker ESP 300E spectrometer in the X-band at a microwave power of 200 μW with a double rectangular TE_{104} mode cavity. The measurement temperatures were 120 and 300 K. Q-band measurements were performed by using a Varian E112 spectrometer at 150 K. The powdered samples were measured after *vacuum* treatment in a quartz tube. Absolute spin concentrations were determined after double integration of the obtained ESR spectra by using $Cu(acac)_2$/KCl (acac = acetylacetonate) mixtures as standards (number of spins: $10^{16}-10^{19}$/g). ESR simulations were performed by simulation programs developed by Mabbs and Collison and written in Fortran 4, processed with a FTN45 conversion package and using NAG library routines.[11] X-ray diffractions (XRD) patterns were recorded using an automated Philips diffractometer with Cu Kα radiation. The materials were

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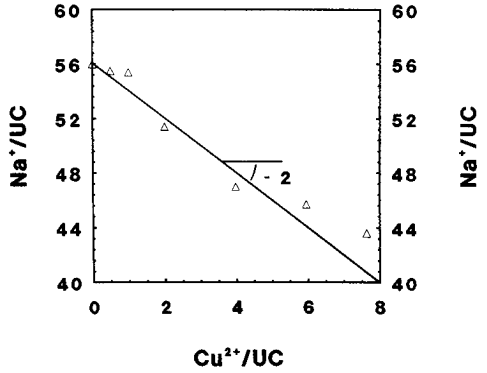


Figure 1. Amount of released Na^+ and immobilized Cu^{2+} complex in zeolite Y with increasing Cu(lysine) complex content in ion exchange solution.

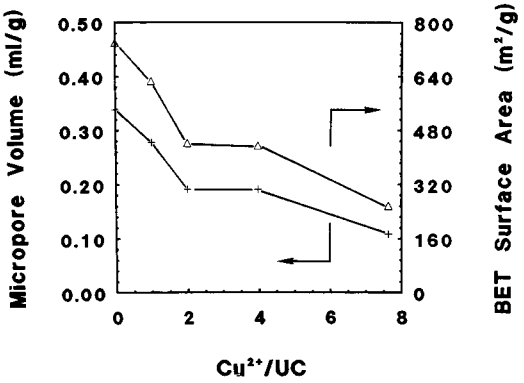


Figure 2. Evolution of the micropore volume and BET surface area with increasing complex loading for Cu(lysine)-exchanged zeolite Y.

loaded in a quartz flow cell with a Suprasil window for diffuse reflectance spectroscopy (DRS). DRS spectra were taken on a Varian Cary 5 UV−vis−NIR spectrophotometer at room temperature. The spectra were recorded against a halon white reflectance standard in the range 2500−200 nm. The computer processing of the DRS spectra consisted of the following steps: (1) subtraction of the baseline, (2) conversion to wavenumber, and (3) calculation of the Kubelka−Munk (KM) function. Atomic absorption spectrometry (AAS) measurements were performed using an Instrumentation Laboratory Inc. apparatus with a nitrous oxide−acetylene flame. The light source was a hollow cathode lamp with a wavelength of 589.6 and 324.7 nm for Na^+ and Cu^{2+}, respectively. The amounts of Na^+ and Cu^{2+} were determined after dissolution of known quantities of zeolite materials in HF/H_2SO_4. The ligand content was determined by the Micro−Kjeldahl method after dissolution of known quantities of solid in 0.05 M Se/H_2SO_4. The ammonia, generated by distillation, was absorbed in 2% boric acid solution, which was then titrated with a sulfuric acid solution of known concentration. Nitrogen adsorption isotherms were measured by dynamic adsorption on an Omnisorp 100 of Coulter. The surface area and micropore volume were determined by applying, respectively, the Brunauer, Emmett, and Teller (BET) method and the *t*-plot method of Lippens and de Boer. Scanning electron micrographs (SEM) were obtained using a JEOL Superprobe 733 instrument.

Results

1. Ion Exchange of $Cu(AA)_n^{m+}$ Complexes. Preformed $Cu(AA)_n^{m+}$ complexes are typically prepared in bidistilled water with an AA:Cu^{2+} ratio of 5 (the AA's investigated are lysine, glycine, alanine, serine, proline, tyrosine, histidine, glutamine, glutamic acid, cysteine, tryptophane, leucine, and arginine). An AA:Cu^{2+} ratio of 5 is experimentally needed because lower ratios give partial hydrolysis of Cu^{2+}, which starts above a pH of 6. As an example, we will discuss the ion exchange process of $Cu(lysine)_n^{m+}$ complexes in zeolite Y at pH 10. By using an increasing amount of preformed $Cu(lysine)_n^{m+}$ complex in bidistilled water together with zeolite Na−Y, we have measured the amount of released Na^+, together with the amount of Cu^{2+} taken up by the zeolite material. This is presented in Figure 1, which shows that the synthesis proceeds via an ion exchange process; about two Na^+ ions of the zeolite are replaced by one Cu^{2+} ion, and consequently, *m* is equal to 2. The N_2 adsorption isotherms of these materials, dehydrated at 110 °C overnight in vacuo (2×10^{-3} Pa), are of Langmuir type I. The evolution of the micropore volume and BET surface area as a function of the $Cu(lysine)_2^{2+}$ loading is presented in Figure 2. The micropore volume decreases almost linearly from 0.33 mL/g for a pure Y zeolite to 0.11 mL/g for the highest $Cu(lysine)_2^{2+}$ loading. Similarly, the zeolite surface is drastically reduced by the uptake of the Cu complexes from 740 m^2/g (pure zeolite Y) to 260 m^2/g. We think that the bend in the curves around $2Cu^{2+}/UC$ is an artifact of the measurement on the sample. Precipitation of $Cu(lysine)_2^{2+}$ crystals was not observed by scanning electron microscopy. All this information suggests that a continuous filling of the micropores of the zeolites by $Cu(lysine)_2^{2+}$ complexes has occurred. In addition, the water content of the samples decreases with increasing amount of exchanged Cu complexes.

In another experiment, materials were prepared by ion exchange of preformed $Cu(AA)_n$ complexes as a function of the solution pH and the type of AA. The obtained solids were chemically and spectroscopically analyzed. No $Cu(AA)_n$ immobilization could be detected for solutions of complexes at a pH of 10 with AA = glycine, alanine, tyrosine, serine, phenylalanine, glutaminic acid, glutamine, histidine, and cysteine, while traces of Cu^{2+} were detected with alanine and phenylalanine (at pH = 6.4) and leucine (at pH = 10) as ligands. Only for lysine, arginine, proline (all at pH = 10) and histidine (at pH = 7.3) as ligands, ion exchange of $Cu(AA)_n^{m+}$ complexes was observed. Thus, the key parameters controlling the ion exchange process are the type of AA and the pH.

2. Spectroscopic Characterization of Immobilized $Cu(AA)_n^{m+}$ Complexes. The ion-exchanged zeolite samples are light blue (histidine) or blue (arginine, lysine, and proline). Independent of the Cu loading and the ligand type (lysine, arginine, proline and histidine), the hydrated $Cu(AA)_n^{m+}$ samples are characterized by absorption bands around 16 000 and 40 000 cm^{-1} in diffuse reflectance spectroscopy and a typical axially symmetric spectrum with hyperfine splitting in electron spin resonance with $g_{||}$ and $g_\perp$ and $A_{||}$ values around, respectively, 2.25, 2.06, and 175 G. This is summarized in Table 1, together with the DRS and ESR parameters of Cu-exchanged zeolite Y as a reference material. The band around 40 000 cm^{-1} is a ligand to metal charge transfer (LMCT).[12] The ESR parameters were obtained by simulation using an axially symmetric Hamiltonian. The spectral features, reported in Table 1, are characteristic of those observed in copper proteins (e.g., galactose oxidase with an absorption at 15 900 cm^{-1} and ESR parameters of $g_{||} = 2.24$, $g_\perp = 2.06$, $A_{||} = 175$ G (hfs), $A_\perp <$ 0.5 G with shfs, and $A_{N\perp} = 15.1$ G) with N and O in the first coordination sphere of Cu^{2+}.[5]

As an example, the DRS and the X- and Q-band ESR spectra of $Cu(lysine)_n^{2+}$ exchanged zeolite Y with 4 Cu/UC are presented in Figure 3. The ESR parameters, obtained by spectral simulation in the X- and Q-band, and the main DRS absorption band are summarized in Table 1 and are indicative of the presence of N ligand(s) in the coordination sphere of Cu^{2+}. The

TABLE 1: ESR Parameters[a] and DRS Absorption Bands of CuY and Immobilized Cu(AA)$_n$ Complexes in Zeolite Y

zeolite	$g_{\|\|}$	$g_\perp$	$A_{\|\|}$ (G)	$A_\perp$ (G)	$A_{\perp,N}$ (G)	d−d absorption (cm^{-1})
$[Cu(H_2O)_6]^{2+}$-Y	2.40	2.09	134	9		12 500
$[Cu(lysine)_2]^{2+}$-Y	2.24	2.06	179	9		16 200
$[Cu(arginine)_2]^{2+}$-Y	2.24	2.06	180	9		16 200
$[Cu(histidine)_2]^{+}$-Y (at low loadings)	2.27	2.06	178	9	13	15 600
$[Cu(histidine)_2]^{+}$-Y (at high loadings)	2.24	2.05	183	9		16 400
$[Cu(proline)^{+}]$-Y (species A)	2.31	2.06	160	9		12 800
$[Cu(proline)^{+}]$-Y (species B)	2.41	2.09	132	9		12 500

[a] The ESR parameters were obtained by simulation, using an axially symmetric Hamiltonian. The values of $g_\perp$ and $A_\perp$ are less accurate because of the presence of overshoot lines, and these values mainly depend on the applied line widths.

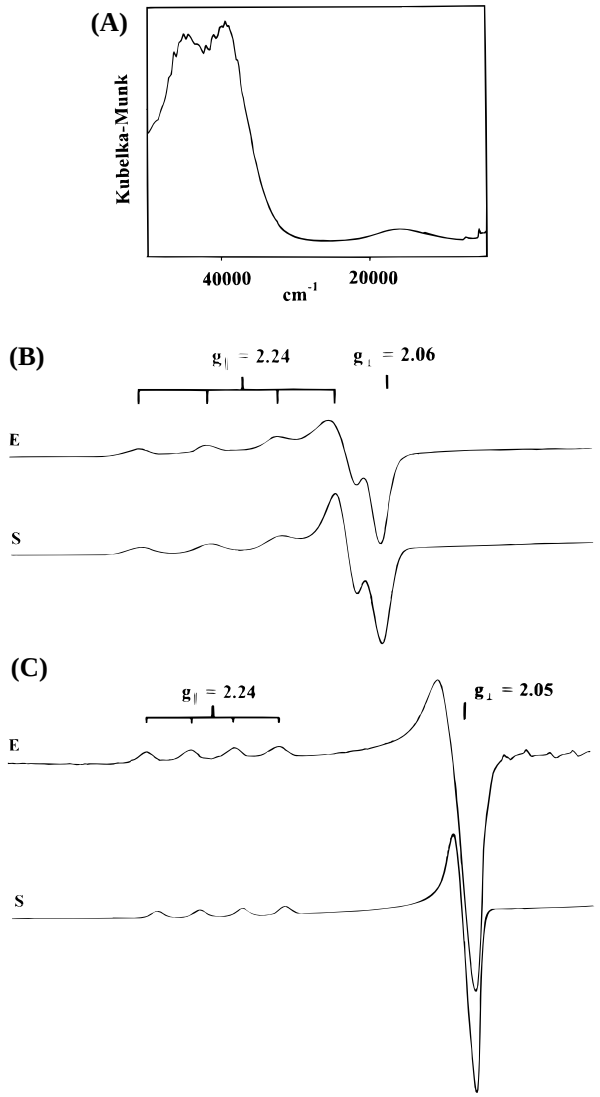


Figure 3. (A) DRS spectrum of exchanged Cu(lysine) in zeolite Y. (B) ESR spectra in X-band of exchanged Cu(lysine) in zeolite Y: (E) experimental spectrum measured at 120 K; (S) simulated spectrum. (C) ESR spectra in Q-band of exchanged Cu(lysine) in zeolite Y: (E) experimental spectrum measured at 150 K; (S) simulated spectrum.

occluded Cu(lysine)$_n^{2+}$ can therefore be envisaged as Cu^{2+} surrounded by two N and two O atoms in a square planar coordination by ligation of two lysine molecules, i.e., Cu(lysine)$_2^{2+}$. The DRS intensity of the d−d absorption band and

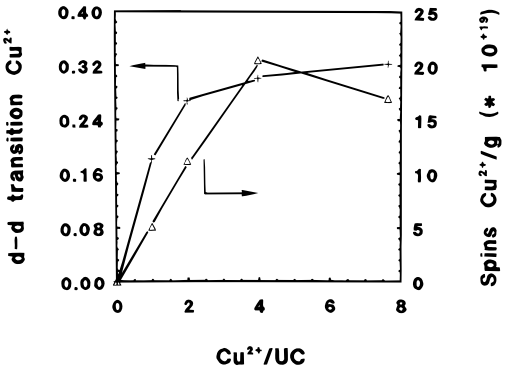


Figure 4. Intensities of Cu^{2+} in DRS and ESR as functions of Cu(lysine) loading in zeolite Y. (The DRS intensities were measured on the band maxima of the d−d transition, and the ESR intensities were obtained after double integration and comparison with a reference compound with known spin density.)

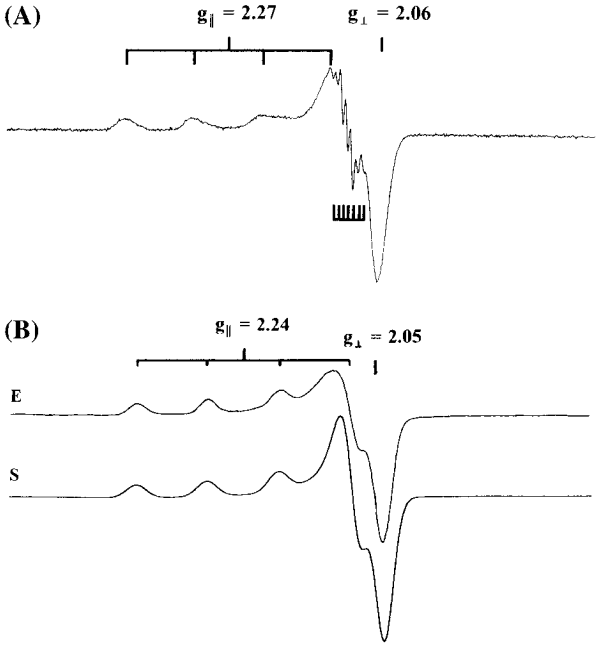


Figure 5. (A) Experimental ESR spectrum in X-band of exchanged Cu(histidine) in zeolite Y at low Cu loadings measured at 120 K. (B) ESR spectra in X-band of exchanged Cu(histidine) in zeolite Y at high Cu loadings: (E) experimental spectrum measured at 120 K; (S) simulated spectrum.

the amount of Cu^{2+}, as determined by quantitative ESR, are given in Figure 4 for increasing Cu(lysine)$_2^{2+}$ loading in zeolite Y. The d−d absorption band of Cu^{2+} increases, although nonlinearly, with increasing Cu loading. This nonlinearity may be due to the difference in water content of the samples and thus to differences in scattering properties of the samples. With ESR, the maximum signal intensity is reached around 4 Cu/UC and at higher Cu(lysine)$_2^{2+}$ loadings; the intensity levels off due to spin−spin interactions. But at small loadings (roughly $\leq 4Cu^{2+}$/UC) there is a good correlation between the intensity increase of the d−d transition and that of the ESR spectrum, suggesting isolated Cu(lysine)$_2^{2+}$ complexes.

The ESR spectra of the Cu(arginine)$_2^{2+}$ complexes are almost identical with those of encaged Cu(lysine)$_2^{2+}$ complexes. The ESR spectra of the occluded Cu(proline)$_n^{m+}$ and Cu(histidine)$_n^{m+}$ are clearly different. The X-band ESR spectrum of Cu(histidine)$_n^{m+}$-Y at low loadings is characterized by a seven-line superhyperfine structure, which is due to three N atoms ($2I_N n_N + 1 = 7$) (see Figure 5A). However, in Q-band ESR and at higher loadings (see Figure 5B) this superhyperfine

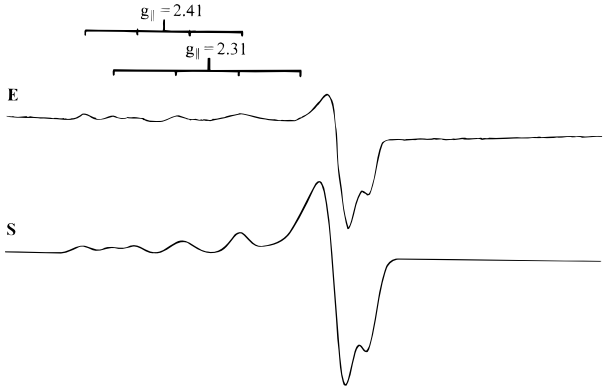


Figure 6. ESR spectra in X-band of exchanged Cu(proline) in zeolite Y: (E) experimental spectrum measured at 120 K; (S) simulated spectrum.

TABLE 2: d−d Transition Band Positions of $Cu(AA)_2^{n+}$ Complexes Encaged in Zeolite Y after Exchange with a Second AA

encaged $Cu(AA)_2^{n+}$ complex with AA =	second AA	DRS absorption band (cm^{-1})
lysine	glycine	16 200
lysine	arginine	16 200
lysine	histidine	16 500
arginine	glycine	16 250
arginine	histidine	16 350
arginine	histidine	16 500

splitting structure is absent. The most probable coordination of Cu^{2+} is by two histidine molecules, one coordinating by two N ligands, while the other coordinates by one O and one N atom. The fourth ligand is thus an oxygen of the carboxy group of histidine, and the complex can be denoted as $Cu(histidine)_2^{+}$. At higher loadings, the d−d absorption band shifts to 16 400 cm^{-1}, $A_{||}$ increases, and $g_{||}$ decreases slightly, suggesting a NNNN coordination around Cu^{2+}. This results in a somewhat stronger ligand field.

The ESR spectrum of ion-exchanged $Cu(proline)_n^{m+}$ is a special case and is composed of two different ESR spectra. This is presented in Figure 6, together with the corresponding simulated spectrum. The simulation procedure consists of three steps: (1) a separate simulation of the two Cu^{2+} signals by using an axially symmetric Hamiltonian with hyperfine splitting, (2) a summation of both simulated spectra with appropriate weight factors, and (3) comparison with the experimental spectra and possible reevaluation of the starting variables and reiteration. The obtained ESR parameters are included in Table 1. The first Cu^{2+} species (species B) has ESR parameters and a d−d band maximum close to those of $Cu(H_2O)_6^{2+}$ in zeolites, while the other Cu^{2+} species (species A) must be coordinated with only one proline ligand, i.e., a $Cu(proline)^{+}$ complex. Such coordination explains the low value of the d−d transition (Table 1). Similar spectral observations are observed when CuY zeolites were exchanged with a solution of an amino acid. Thus, ion exchange of AA with pre-exchanged Cu zeolites gives rise to an incomplete complexation of Cu^{2+}, in that $Cu(H_2O)_6^{2+}$ coexists with $Cu(AA)_n^{m+}$.

In another experiment, pre-exchanged $[Cu(lysine)_2^{2+}]$-Y and $[Cu(arginine)_2^{2+}]$-Y samples were suspended in an aqueous solution with or without AA (glycine, arginine, lysine, and histidine) at pH 10. The obtained solids were measured by DRS, and the main absorption bands are given in Table 2. Spectral shifts to higher wavenumber are only obtained with histidine. Thus, histidine is the only AA capable of replacing lysine and arginine in the coordination sphere, creating thereby a NNNN-type coordination in the plane. In addition, the intensity of the d−d band decreases and the solution after exchange was blue. Both observations are indicative of the leaching of Cu(histidine) complexes in solution.

TABLE 3: Catalytic Performances of $Cu(histidine)_2^{+}$ Complexes Encaged in Zeolite Y at 60 °C[a,b]

substrate	time (h)	conversion (TON[c])	selectivity (mol %)
cyclohexane	24	450	cyclohexanol (50) cyclohexanone (50)
benzyl alcohol	24	2421	benzoic acid (33) benzaldehyde (66)
1-pentanol	24	1425	pentanoic acid (100)
cyclohexene	24	3230	cyclohexenoxide (9) 1,2-cyclohexanediol (89) cyclohex-2-en-1-ol (0.3) cyclohex-2-en-1-one (1.7)

[a] 100 mmol substrate, 150 mmol oxidant *tert*-butyl hydroperoxide. [b] No Cu^{2+} leaching during reaction, as determined by AAS. [c] TON = turnover number.

Drying of the ion-exchanged samples results in the removal of water and only a slight shift in the DRS absorptions and ESR parameters. Furthermore, all the occluded $Cu(AA)_2^{m+}$ complexes are thermally stable up to 100 °C. In the case of histidine, admission of ammonia onto the dried sample at room temperature results in the formation of a $Cu(histidine)_2(NH_3)_x$ complexes with absorption at 16 000 cm^{-1}, up 500 cm^{-1} from 15,600 cm^{-1}, and $g_{||}$, $g_{\perp}$, and $A_{||}$ values at, respectively, 2.26, 2.07, and 160 G. In addition, the super hyperfine splitting disappeared because of a distortion of the complex. Evacuation of the ammonia at 50 °C leads to the initial Cu^{2+} state, and this process is totally reversible. Thus, by simple evacuation, a free coordination site is created in the $[Cu(histidine)_2^{+}]$-Y system, necessary for catalysis.

Catalytic Characterization of Immobilized $Cu(AA)_n^{m+}$ Complexes. The oxidation of alcohols, alkanes, and alkenes in the presence of $Cu(histidine)_2^{+}$ in zeolite Y with *tert*-butyl hydroperoxide has been studied at 60 °C in batch-type reactors. The catalytic performances of $[Cu(histidine)_2]^{+}$-Y with 0.75 Cu/UC are summarized in Table 3. 1-Pentanol is oxidized to pentanoic acid with a selectivity of 100%, while the oxidation of benzyl alcohol gives both benzaldehyde and benzoic acid in a ratio of about 2:1. Equal selectivities toward cyclohexanol and cyclohexanone are observed in the oxidation of cyclohexane. However, the conversion is lower. The best catalytic results were obtained for the epoxidation of cyclohexene. At a turnover of 3230, the major reaction product is 1,2-cyclohexanediol. This product is formed from the hydrolysis of cyclohexenoxide on some acid sites of zeolite Y. A minor allylic oxidation is also observed, indicative of only traces of free copper. After reaction, no free Cu ions were detected in the reaction mixture and combined ESR−DRS spectroscopies show also that the $[Cu(histidine)_2]^{+}$ complexes are maintained inside the cages of zeolite Y. Furthermore, after repeated generation (three times), no changes in catalytic and spectroscopic properties could be observed.

Table 4 compares the catalytic activity in cyclohexene oxidation of zeolite-encaged $Cu(AA)_2^{n+}$ complexes as a function of the type of AA. Although the activity is much lower and the allylic oxidation is more pronounced for encaged $Cu(lysine)_2^{2+}$ and $Cu(arginine)_2^{2+}$ complexes, the same oxidation products and overall stability are obtained as with the $[Cu(histidine)_2^{+}]$-Y system. The lower activity can probably be explained by the less stable coordination geometries of the encapsulated complexes (NNOO for $Cu(lysine)_2^{2+}$ and $Cu(arginine)_2^{2+}$ *versus* NNNO or NNNN for $Cu(histidine)_2^{+}$). In summary, novel catalytically active and stable materials have

TABLE 4: Catalytic Performances of $Cu(AA)_2^{n+}$ Complexes Encaged in Zeolite Y in Cyclohexene Oxidation at 60 °C

encaged $Cu(AA)_2^{n+}$ with AA =	time (h)	conversion (TON)	selectivity (mol %)
histidine	24	3230	cyclohexenoxide (9)
			1,2 cyclohexanediol (89)
			cyclohex-2-en-1-ol (0.3)
			cyclohex-2-en-1-one (1.7)
lysine	24	735	cyclohexenoxide (10)
			1,2 cyclohexanediol (84)
			cyclohex-2-en-1-ol (1.5)
			cyclohex-2-en-1-one (4.5)
arginine	24	669	cyclohexenoxide (8)
			1,2 cyclohexanediol (85)
			cyclohex-2-en-1-ol (2)
			cyclohex-2-en-1-one (5)

been designed for the oxidation of organic compounds in the presence of peroxides at relatively low temperatures.

Discussion

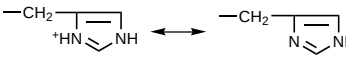
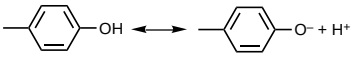
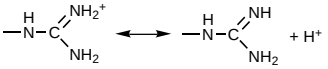
In the present investigation, the ion exchange process of preformed transition-metal-ion−amino acid complexes in zeolites has been studied—according to the authors' knowledge—for the first time. Cu^{2+} was chosen as the transition metal ion of choice because it forms, according to the Irving−Williams series, the most stable coordination complexes.[13] In addition, Cu^{2+} complexes can be easily studied by electron spin resonance and diffuse reflectance spectroscopy in the UV−vis−NIR region.[14] The coordination complexes of Cu^{2+} typically consist of four nearby donor atoms arranged approximately in a plane around the metal ion, with the possibility of one or two more distant axial donors.[13] Amino acids (AA), potentially as bi- or tridentate ligands, can offer N (α-amino, ϵ-amino, or imidazole), O (carboxylate or hydroxyl), and S (sulfhydryl) as donor atoms, and the exact composition of the first coordination sphere around Cu^{2+} mainly depends on the solution pH, the Cu^{2+}:AA ratio, and the type of AA.[13,15] In this work, the AA:Cu^{2+} ratio in the exchange solution was kept constant at 5, and the influence of the pH and the type of AA on the coordination geometry of the occluded Cu^{2+} complexes was studied in detail. The aim of this discussion is then (1) to discuss the ion exchange process of $Cu(AA)_n^{m+}$ complexes in zeolites, (2) to compare the coordination chemistry of occluded $Cu(AA)_n^{m+}$ complexes with that in solution, and (3) to discuss the catalytic potential of the synthesized materials.

1. Ion Exchange Process. The ability of a preformed $Cu(AA)_n^{m+}$ complex for ion exchange strongly depends on its charge and stability, which are both solution pH dependent. The stability and overall charge of $Cu(AA)_n^{m+}$ complexes in solution can be explained by taking into account the p*K* values of the various donor groups of amino acids, which are presented in Table 5.[15]

The investigated AA can be divided into three groups on the basis of our ion exchange results. The first group consists of α-amino acids with no functional group or with a OH, SH, or COOH group in their R chain. The second group consists of AA containing a basic amino R group, whereas the third group has only one member, i.e., the cyclic amino acid proline.

In the case of α-amino acids with no functional group in the R chain (alanine, glycine, leucine, and phenylalanine) at pH 10, two amino acids will coordinate around Cu^{2+} in a glycine-like way, giving rise to a stable NNOO coordination. The charge of the formed complex is zero because the two positive charges of Cu^{2+} are neutralized by the two carboxylate groups of the AA. Indeed, both terminal carboxyl and amino groups

TABLE 5: p*K* Values of Ionizable Groups in Amino Acids[15]

group or AA	acid ↔ base + H^+	p*K*
terminal carboxyl	$-COOH \leftrightarrow -COO^- + H^+$	3.1
aspartic and glutamic acid	$-COOH \leftrightarrow -COO^- + H^+$	4.4
histidine		6.5
terminal amino	$-NH_3^+ \leftrightarrow -NH_2 + H^+$	8.0
cysteine	$-SH \leftrightarrow -S^- + H^+$	8.5
tyrosine		10.0
lysine	$-NH_3^+ \leftrightarrow -NH_2 + H^+$	10.0
arginine		12.0

are in their base form, and neutral complexes, unsuitable for ion exchange, are formed (Table 5). By decrease of the pH below 8, the terminal NH_2 of the AA will become positively charged. The AA loses its chelating property, and consequently, the complexes will become less stable. Cu^{2+} can then be exchanged as a hexaquo complex on the zeolite, as is observed for phenylalanine and alanine at pH = 6.4. In the case of α-amino acids with a hydroxyl group (tyrosine and serine), sulfhydryl group (cysteine), or a carboxyl group (glutaminic acid), negatively charged complexes are formed at relatively high pH because the functional groups are dissociated (Table 5). Such preformed complexes, although relatively stable, are not suitable for cation exchange.

Amino acids with a basic amino R group (lysine, arginine, and histidine) may serve as tridentate ligands. They form stable and positively charged Cu complexes at relatively high pH. In the case of lysine, the α-amino group is positively charged at around pH 10, giving the Cu complex a net positive charge of 2. The same holds for arginine, while the situation is more complicated for histidine.[4] At pH 7.5, two histidine ligands are coordinated to Cu^{2+}, one in a glycine-like way, the other in a histamine-like way. In addition, one carboxylate group coordinates in an apical position and the formed complex with NNNO coordination has a net positive charge of 1. The formed complex is then in equilibrium with another complex in which both histidine molecules are coordinated in a histamine-like way. At pH 10, however, the imidazole ring loses its positive charge and neutral complexes are formed. This explains why the Cu-(histidine)$_2$ complexes cannot be ion exchanged around pH 10.

The repertoire of amino acids also contains a special amino acid, proline. Proline is a cyclic amino acid because its aliphatic side chain is bonded to both the nitrogen and α-carbon atoms.[15] Its imino group starts deprotonating around pH 8, and strong Cu complexes, suitable for ion exchange, are formed at pH 10.

In summary, $Cu(AA)_n^{m+}$ complexes can only be exchanged on a zeolite if (1) its stability is high enough and (2) the pH of the exchange solution is adapted in such a way that the functional groups of the R chain are positively charged. Low complex stability may lead to the ion exchange of $Cu(H_2O)_6^{2+}$, whereas Cu zeolites brought in contact with AA give rise to incomplete Cu^{2+} complexation. Thus, amino acid and zeolite act as ligands, both competing for complexation with Cu^{2+}.

2. Coordination Chemistry and Catalytic Potential. The composition of the first coordination sphere around Cu^{2+} can be altered by changing the type of AA and the Cu loading. The following coordination compositions were designed around Cu^{2+}: NNNN (with histidine as AA at higher Cu loadings), NNNO (with histidine as AA at lower Cu loadings), NNOO (with lysine or arginine as AA), and NOOO (with proline as AA). Water molecules, lattice oxygens, and additional amino

TABLE 6: Catalytic Performances of Different Zeolite-Based Catalysts in Cyclohexene Oxidation

catalyst	amount (g)	feed (mmol)	oxidant	temperature (°C)	time (h)	substrate conversion (%)	turnover rate (h^{-1})	ref
Mn(salen)/Y	0.1	0.2	PhIO		16	55	2	16
Ti-β	0.2	33	H_2O_2	25	3.5	2	4	17
Ti-silicalite	0.2	33	H_2O_2	25	3		1	17
Cu(histidine)-Y	0.15	100	TBHP	60	24	28	135	this work

and carboxy groups of the chelating amino acids may coordinate Cu^{2+} in the axial position, giving rise to tetragonally distorted octahedral complexes. This axial interaction is weak, and the ligands can be replaced by ammonia. In addition, the synthesized coordination geometries are essentially the same as those in solution. Thus, the zeolite has only a minor effect on the coordination geometry of the encapsulated $Cu(AA)_n^{m+}$ complexes and the complexes have a coordination geometry quasi-identical with their analogues in solution.

The catalytic activity of the most active material, the Cu-(histidine)$_2^+$-Y system, is compared in Table 6 with recent literature results in cyclohexene oxidation.[16,17] Although comparison is difficult because the oxidants and temperature are different, the data clearly show that the prepared materials are competitive with known systems. Furthermore, we have obtained turnover numbers (TON) of 1−2 per min, which are about the same as that of several natural enzymes (0.5−5 TON per minute).[18] Thus, the obtained catalytic performances confirm the great potential and chemistry of these novel materials.

Conclusions

We have demonstrated that Cu(histidine)$_2^+$, Cu(lysine)$_2^{2+}$, Cu(arginine)$_2^{2+}$, and Cu(proline)$^+$ complexes can be encapsulated in NaY zeolites by a simple ion exchange procedure. The ion exchange process is mainly determined by the solution pH, which controls the stability and the charge of the preformed Cu complexes. The physical properties of zeolites are altered by introducing $Cu(AA)_n^{m+}$ complexes; the pore volume, the surface area, and the hydrophilicity of the zeolite decrease with increasing amount of occluded complexes. The composition of the first coordination sphere around Cu^{2+} can be changed from NNNN to NOOO by varying the type of amino acid. A zeolite acts as a ligand and competes with amino acids for complexation with Cu^{2+}. Zeolites have only minor influence on the local geometry of encapsulated Cu complexes, and its coordination chemistry is almost identical with that in solution.

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References

(1) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Amino Acids; Plenum Press: New York, 1974; Vol. 1.

(2) Sakurai, T.; Yamauchi, O.; Nakahara, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3203.

(3) Nadhim, A. A. An Experimental Study of the Complexation between Cu(2+) and Some α-Amino Acids with Emphasis on Stereoselective Effects. Ph.D. Thesis, Uppsala University, 1984.

(4) Sigel, H.; McCormick, D. B. *J. Am. Chem. Soc.* **1971**, *93*, 2041.

(5) Lontie, R. *Copper Proteins and Copper Enzymes*; CRC Press, Inc.: Boca Raton, FL, 1984; Vols. 1−3.

(6) Murphy, B. P. *Coord. Chem. Rev.* **1993**, *124*, 63.

(7) Beinert, H. *Coord. Chem. Rev.* **1977**, *23*, 119.

(8) Parton, R. F.; De Vos, D.; Jacobs, P. A. In *Zeolite Microporous Solids: Synthesis, Structure, and Reactivity*; Derouane, E. G., et al., Eds., Kluwer: Amsterdam, 1992; p 555

(9) De Vos, D. E.; Knops-Gerrits, P. P.; Parton, R. F.; Weckhuysen, B. M.; Jacobs, P. A.; Schoonheydt, R. A. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1995**, *21*, 185.

(10) Weckhuysen, B. M.; Verberckmoes, A. A.; Vannijvel, I. P.; Pelgrims, J. A.; Buskens, P. L.; Jacobs, P. A.; Schoonheydt, R. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2652.

(11) Collison, D.; Mabbs, F. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1565. Mabbs, F. E.; Collison, D. *Electron paramagnetic resonance of d transition metal compounds*; Elsevier Science Publishers B. V.: Amsterdam, 1992.

(12) Wilson, E. W.; Kasperian, M. H.; Martin, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 5365.

(13) Williams, D. R. *The metals of life: the solution chemistry of metal ions in biological systems*; Van Notrand Reinhold Company: London, New York, 1971.

(14) Schoonheydt, R. A. *Catal. Rev. Sci. Eng.* **1993**, *35*, 129.

(15) Stryer, L. *Biochemistry*, 3rd ed.; W. H. Freeman and Company: New York, 1988.

(16) Bowers, C.; Dutta, B. K. *J. Catal.* **1990**, *122*, 271.

(17) Corma, A.; Comblar, M. A.; Esteve, P.; Martinez, A.; Pérez-Pariente, J. *J. Catal.* **1994**, *145*, 151.

(18) Mansuy, D.; Battioni, P. In *Activation and Function of Alkanes*; Hill, C. L., Ed.; Wiley: New York, 1989; pp 195−218.

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