

with N_2 , and sealed with a rubber septum. After 50 μ L of decane (internal standard, weighed to 0.1 mg) and 10 mL of ether were added, it was cooled to $-50^\circ C$, and 1.00 mmol of BuLi (Aldrich, ~ 1.5 M solution in hexanes, standardized immediately before use) was added. After 0.5 h at $-50^\circ C$, a 1.0-mL sample was withdrawn by using a syringe cooled with dry ice,¹⁶ and it was injected into excess benzoyl chloride in a 2-dram vial that had been purged with N_2 and sealed with a rubber septum. The vial was cooled in dry ice until the sample had been injected, and then it was allowed to warm to room temperature. The reaction mixture was transferred to a $-25^\circ C$ bath for 0.5 h and the sampling repeated. It was likewise sampled after 0.5 h at $0^\circ C$ and 0.5 h at $25^\circ C$. The amount of viable cuprate remaining at each stage was equated with the amount of 1-phenyl-1-pentanone present in the samples taken, as measured by calibrated GLC. For the copper reagent from 1 and BuLi, the yields were 100% ($-50^\circ C$), 90% ($-25^\circ C$), 85% ($0^\circ C$), and 57% ($25^\circ C$).

Registry No. 1, 97877-83-3; 2, 97877-82-2.

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The Tetraamminecopper(II) Complex in Zeolite Y. A Raman Spectroscopic Study

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Received January 11, 1985

In recent years there has been much interest in the structure and catalytic properties of transition-metal ions and complexes in zeolites.¹ The zeolite matrix can influence the reactivity of metal complexes by the unique steric and electrostatic constraints its cavities can impose. Many spectroscopic studies, including infrared,² EPR,³ EXAFS,⁴ and XPS,⁵ have been explored to study the bonding of metal complexes within zeolite cavities. Raman spectroscopy, which provides considerable structural information on coordination compounds, has not been exploited for study of metal-zeolite systems, mainly because of the high fluorescence from the matrix.

This preliminary report indicates that, by careful manipulation of metal-zeolite complexes, it is possible to obtain bonding information by spontaneous Raman spectroscopy. We have studied the copper-ammine system because of the extensive EPR⁶ and electronic spectroscopic⁷ information on these complexes in zeolites. Also, these complexes are active intermediates in the catalytic oxidation of ammonia.⁸ It is important to point out that IR spectroscopy of these systems is not very valuable in the low-frequency region, where metal-ligand vibrations are expected.

Experimental Section

Cu-Y zeolite was prepared by ion exchanging zeolite Y (Union Carbide LZY 52) with 0.1 M $Cu(NO_3)_2$ solution. The Cu loading was determined by atomic absorption to be 7.3% by weight.

Pellets of Cu-Y were activated in a greaseless vacuum system by using the procedure described by Lunsford and co-workers.⁶ To keep the fluorescence to a minimum, it is important to start the activation at low temperature ($100^\circ C$) and gradually increase it stepwise at $100^\circ C/h$ to $400^\circ C$. Ammoniation was carried out with anhydrous NH_3 (Matheson)

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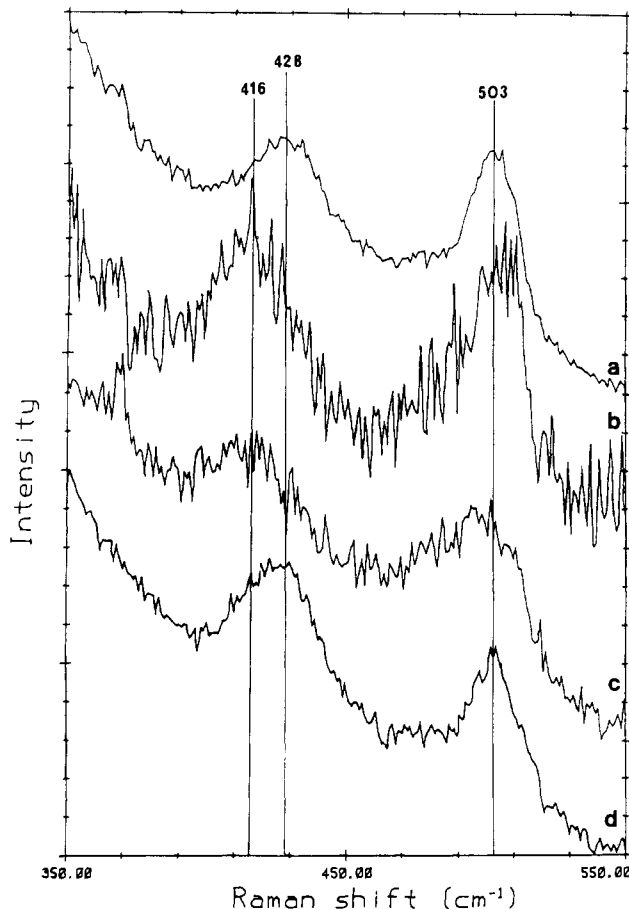


Figure 1. Raman spectra in the Cu-N stretching region: (a) hydrated ion-exchanged $Cu(NH_3)_4^{2+}$ -Y; (b) dehydrated $CuY + NH_3$; (c) dehydrated ion-exchanged $Cu(NH_3)_4^{2+}$ -Y; (d) hydrated $CuY + NH_3$. Laser line = 457.9 nm.

at an ammonia pressure of 400 torr. The pellets were transferred anaerobically to an enclosed Raman spinning cell. The hydration of these samples was carried out over a saturated NH_4Cl solution. The samples were bright blue, with an absorption maximum at ~ 625 nm.

Ion exchange of Na-Y was carried out with 0.1 M $Cu(NH_3)_4(NO_3)_2$ solution⁹ in 1.5 M NH_4OH for 48 h (Cu by weight 5.6%). The washed sample was hydrated over saturated NH_4Cl solution. Dehydration of this sample was carried out by heating at $135^\circ C$ for 1 h at 10^{-5} torr, it was ammoniated at 500 torr of NH_3 for 20 min, and the process was repeated four times.

Raman spectra were collected by using a Spex 1403 double monochromator with an RCA C31034 GaAs photomultiplier and photon-counting electronics. The samples were excited with 50-100 mW of the 457.9-nm line of an argon ion laser. Similar spectra were also observed at 514.5 nm. Spectra were scanned in 1-cm^{-1} steps with collection times of 5 s/wavenumber. All solid samples were spun to avoid any photochemical decomposition and spectra recorded in a 90° configuration. Fluorescence from the zeolite was minimized by working with high-purity chemicals, a greaseless vacuum system, and no contact with plastic ware. The elemental analysis indicates that the concentration of the metal complex in the zeolite that scatters the Raman light corresponds to a solution concentration of 1 mM. The Raman spectra shown in Figure 1 and 2 can be considered as spontaneous Raman spectra (since there are no electronic bands in the vicinity of the laser excitation) and clearly illustrate that, with careful sample handling, it will be possible to obtain Raman spectra of complexes in zeolites at millimolar concentrations. It is important to point out that, for complexes with accessible electronic transitions, resonance-enhanced Raman spectra should provide considerable enhancement in S/N .

Results and Discussion

Lunsford and co-workers, on the basis of EPR and infrared titration studies, have shown that the complex formed by exposing

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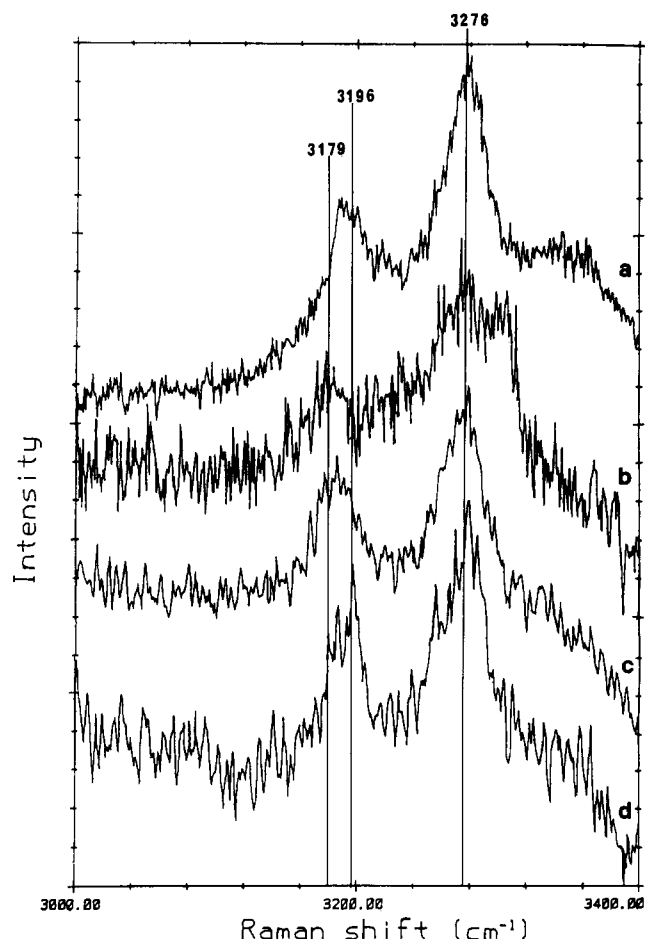


Figure 2. Raman spectra in the N-H stretching region: (a) hydrated ion-exchanged $\text{Cu}(\text{NH}_3)_4^{2+}\text{-Y}$; (b) dehydrated $\text{CuY} + \text{NH}_3$; (c) dehydrated ion-exchanged $\text{Cu}(\text{NH}_3)_4^{2+}\text{-Y}$; (d) hydrated $\text{CuY} + \text{NH}_3$. The intensity scale is half that in Figure 1. Laser line = 457.9 nm.

dehydrated Cu-Y to NH_3 in the gas phase is the square-planar $\text{Cu}(\text{NH}_3)_4^{2+}$ ion.^{6,10} However, there is some controversy about the location of these complexes in the supercages or sodalite cages of the zeolite. Vadrine et al., on the basis of the temperature dependence of hyperfine coupling, have proposed that $\text{Cu}(\text{NH}_3)_4^{2+}$ can be formed in the sodalite cage by migration of NH_3 through the six-membered rings (diameter 2.2 Å).¹¹ However, from a comparison of the size of the sodalite cage vs. that of the complex, considerable H bonding can be expected in the smaller cages. The $\text{Cu}(\text{NH}_3)_4^{2+}$ complex ion can also be exchanged into zeolite Y but will be too large to enter the sodalite cage and must be located in the supercages. We have investigated the Raman spectra of the copper ammine complex under both these conditions.

The Raman spectra of $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ in solution and solid state were investigated and provide a convenient reference for studying the complexes in zeolite Y. Exhaustive studies of the vibrational spectra of metal-ammine complexes, in general, suggest that the vibrations can be separated into skeletal vibration involving the metal-nitrogen bonds and the vibration of the ligand NH_3 , since the coupling between them is minimal.¹² Preliminary Raman spectra of $\text{Cu}(\text{NH}_3)_4^{2+}$ reported by Damaschun¹³ and Müller and co-workers¹⁴ only showed a weak band at 375 cm^{-1} , assigned to $\nu(\text{Cu-N})$ (B_{1g}), and a stronger band at ~ 420 cm^{-1} due to $\nu(\text{Cu-N})$ (A_{1g}). For $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ in the solid state, we observe bands at 303 cm^{-1} ($\delta(\text{NCuN})$, B_{2g}), 428 cm^{-1} ($\nu_s(\text{Cu-N})$, A_{1g}), 790 cm^{-1} ($\rho_r(\text{NH}_3)$, B_{2g}), 1249 and 1300 cm^{-1} ($\delta_s(\text{HNNH})$, A_{1g} ,

B_{1g}), 3195 cm^{-1} ($\nu_s(\text{N-H})$, A_{1g}), and 3260 cm^{-1} ($\nu_{as}(\text{N-H})$, B_{2g} , E_g). All of these bands were also observed in solution except for the NH_3 stretching modes, due to the strong interference from the H_2O bands. The strongest bands in the Raman spectrum were $\nu_r(\text{Cu-N})$ and $\nu(\text{N-H})$ modes. We have therefore used these bands to evaluate the influence of the zeolite on the $\text{Cu}(\text{NH}_3)_4^{2+}$ complexes within its cavities.

In Figure 1a,b are compared the Raman spectra of $\text{Cu}(\text{NH}_3)_4^{2+}$ ion exchanged into the zeolite and formed by exposing dehydrated Cu-Y to NH_3 in the Cu-N stretching region. The band at ~ 503 cm^{-1} is due to the zeolite. The Raman spectrum shows that the Cu-N stretching frequency of the ion-exchanged complex at 428 cm^{-1} is similar to that of the complex in aqueous solution, whereas the $\text{Cu}(\text{NH}_3)_4^{2+}$ formed by exposure of NH_3 to Cu-Y exhibits this band at 416 cm^{-1} . Vadrine et al.¹¹ have reported a band at 317 cm^{-1} due to a Cu-N stretch from far-IR studies of a sample of Cu-Y exposed to NH_3 . We do not observe any bands at this frequency. They suggested that this shift in frequency of the 428- cm^{-1} band was due to formation of $\text{Cu}(\text{NH}_3)_4^{2+}$ in the sodalite cages and strong H-bond formation with the zeolitic oxygens. This observation is however contrary to the vibrational changes that are known to occur upon hydrogen bonding.¹² It is a well-accepted fact that, upon increase of H bonding in metal-ammine complexes, there is a decrease in N-H stretching frequencies and an increase in metal-nitrogen stretching frequencies and NH_3 rocking modes.¹⁵⁻¹⁷ Such effects are typically observed in all H-bonded systems; e.g., in associated carboxylic acids the O-H stretching decreases in frequency and C-O stretch increases in frequency. Therefore, an increase in H bonding, as would be expected for $\text{Cu}(\text{NH}_3)_4^{2+}$ in the sodalite cage, would increase the Cu-N stretching frequency.

We investigated the possibility of hydrogen bonding by examining the internal modes of the ligand. We were unable to observe the rocking modes of NH_3 in the metal-zeolite complex but were able to study the N-H stretching frequencies, which are shown in Figure 2a,b. For $\text{Cu}(\text{NH}_3)_4^{2+}$ ion exchanged into zeolite Y the bands are at 3195 cm^{-1} ($\nu_s(\text{N-H})$) and 3278 cm^{-1} ($\nu_{as}(\text{N-H})$), whereas for the complex formed by exposing Cu-Y to NH_3 the bands are at 3179 and 3276 cm^{-1} (a shoulder is also observed at 3300 cm^{-1} , the origin of which is presently not understood). A decrease of ~ 16 cm^{-1} in the N-H symmetric stretching frequency is indicative of H-bond formation, but it is a relatively weak bond. For example, in cobalt(III) hexaammine, when the anion is changed from ClO_4^- to Cl^- , there is a decrease of 130 cm^{-1} in the stretching frequency due to stronger H-bond formation.¹⁵ These results tend to support the conclusion of Lunsford and co-workers⁶ that the $\text{Cu}(\text{NH}_3)_4^{2+}$ ions formed by exposing Cu-Y to NH_3 are in the supercages. Therefore, the decrease in the Cu-N stretching frequency of the $\text{CuY} + \text{NH}_3$ complex as compared to that of ion-exchanged $\text{Cu}(\text{NH}_3)_4^{2+}\text{-Y}$ must arise from some effect other than H bonding.

The influence of water inside the zeolite cavity was investigated by dehydrating a sample of ion-exchanged $\text{Cu}(\text{NH}_3)_4^{2+}\text{-Y}$ and by hydrating a $\text{Cu-Y} + \text{NH}_3$ sample, the Raman spectra of which are shown in Figures 1c,d and 2c,d. On hydration of $\text{CuY} + \text{NH}_3$, the 416- cm^{-1} band moves to 428 cm^{-1} (Figure 1c), and on dehydration of ion-exchanged $\text{Cu}(\text{NH}_3)_4^{2+}\text{-X}$ the 428- cm^{-1} band moves to 418 cm^{-1} (Figure 1d). In the N-H stretching region, the 3179- cm^{-1} band of $\text{Cu-Y} + \text{NH}_3$ moves to 3195 cm^{-1} on hydration and the opposite effect is observed on dehydration of $\text{Cu}(\text{NH}_3)_4^{2+}\text{-Y}$. These results suggest that the absence of H_2O from the zeolite cavity is bringing about the vibrational changes—an increase in hydrogen bonding of NH_3 with the framework oxygens and a decrease in the Cu-N stretching frequency.

Using a simple valence force field model, we estimate a decrease of $\sim 6\%$ in the Cu-N force constant on dehydration. The force

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constant, though really a measure of the curvature near the potential well, bears a linear relationship with the dissociation energy, which is a measure of the depth of the potential energy well. Such a relationship has been confirmed for hexaamminemetal complexes, for which good thermochemical data exist.¹² Also, ligand field stabilization energy and formation constants decrease with a decrease in force constant, but the relationships are more complex.¹⁸ Therefore, the decrease in the Cu-N force constant on dehydration suggests that the electrostatic field of the zeolite destabilizes the $\text{Cu}(\text{NH}_3)_4^{2+}$ complexes in its cavities in the absence of mediation from water. This is in contrast to complex formation in layer clays, where enhanced stabilization has been noted for formation of $\text{Cu}(\text{en})_2^{2+}$ complexes.¹⁹ The decrease in ligand field stabilization energy is also reflected in the electronic absorption spectrum; e.g., $\text{Cu}(\text{NH}_3)_4^{2+}$ in solution has d-d bands at $16\,600\text{ cm}^{-1}$ compared to $15\,600\text{--}16\,300\text{ cm}^{-1}$ in zeolites X and Y.⁷

The electrostatic interaction between the zeolitic framework and the metal complex is considerably greater in the absence of water. This field must then polarize the Cu-N bond leading to a copper-ammine complex with a lower bond order. Richardson noted such field effects in the EPR spectra of Cu-faujasites.²⁰ These effects are very important for understanding the role of zeolite as an active support in the catalysis by transition-metal complexes within its cavities. This preliminary study indicates that Raman spectroscopy can play a role in elucidating such effects.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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Studies of Antimony(III) in Ambient-Temperature Ionic Liquids

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Received November 1, 1984

In previous work¹⁻⁴ we showed the advantage of using a neutral $\text{AlCl}_3\text{-RCl}$ ionic liquid composed of equimolar amounts of AlCl_3 and RCl ($\text{R}^+ = N\text{-}1\text{-butylpyridinium}$ (BuPy^+), $1\text{-methyl-}3\text{-ethylimidazolium}$ (Im^+)) to investigate a variety of chemical and electrochemical reactions.

In this note we study the behavior of Sb(III) under conditions where the unbuffered properties of this neutral melt play an important role.

Experimental Section

$N\text{-}1\text{-Butylpyridinium}$ chloride and $1\text{-methyl-}3\text{-ethylimidazolium}$ chloride and the neutral $\text{AlCl}_3\text{-RCl}$ melts were prepared as previously described.^{1,5,6}

SbCl_3 (Alpha Products, anhydrous) was used without further purification.

The reference electrode was an Al wire (5N Alfa Inorganic) immersed in a 1.5:1 $\text{AlCl}_3\text{-RCl}$ melt, and all potentials are given with respect to

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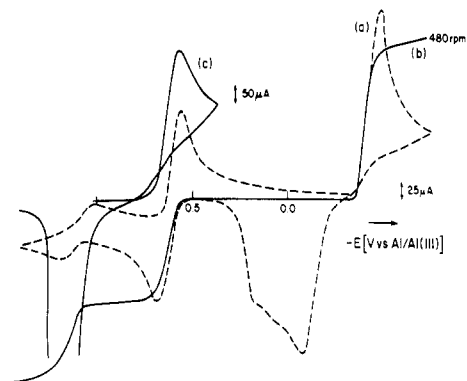


Figure 1. Comparison of electrochemical behavior of Sb(III) in slightly basic (a, b) and slightly acidic (c) $\text{AlCl}_3\text{-ImCl}$ melts (tungsten electrode (area = 0.0784 cm^2); $T = 305\text{ K}$): (a) cyclic voltammogram for $33.1\text{ mmol dm}^{-3}\text{ Sb(III)}$, $v = 0.05\text{ V s}^{-1}$ (b) RDE voltammogram for $33.1\text{ mmol dm}^{-3}\text{ Sb(III)}$ at 480 rpm ; (c) cyclic voltammogram for $42\text{ mmol dm}^{-3}\text{ Sb(III)}$ at $v = 0.05\text{ V s}^{-1}$.

this electrode. The auxiliary electrode was also a coiled Al wire. The essential details of the experimental techniques, electrodes, and operations in the drybox (Vacuum Atmospheres Co.) have been presented previously.⁷

Working electrodes were glassy-carbon disk (area = 0.454 , 0.196 , and 0.071 cm^2), tungsten (0.078 cm^2), and platinum (0.049 and 0.12 cm^2). The electrodes surface preparation procedure has been described previously.⁸

Results and Discussion

Complexation of Sb(III) in $\text{AlCl}_3\text{-RCl}$ Melts. Electrochemical studies of Sb , Sb(III) , and Sb(V) carried out in molten mixtures of AlCl_3 and BuPyCl as a function of melt composition have been presented.⁹ In melt compositions that are basic (mol of AlCl_3 :mol of $\text{RCl} < 1$) both voltammetric and potentiometric studies indicate SbCl_4^- formation. From potentiometric measurements, SbCl_2^+ was indicated as the dominant species in the acidic melts (mol of AlCl_3 :mol of $\text{RCl} > 1$).

Implicit in the use of potentiometry to study the stoichiometry of complexation in $\text{AlCl}_3\text{-RCl}$ melts is the assumption that complexation of the metal ion exclusively involves interaction with chloride ions whereas the interactions with other ligands, AlCl_4^- and Al_2Cl_7^- , are neglected.⁴

To obtain additional information on the complexation of Sb(III) in acidic melts, we employed studies in "neutral" melts.^{1,2,4} It is important, however, to emphasize two characteristic features of the Sb(III)/Sb system. The Stokes-Einstein parameter, $D\eta/T$, (where D , η , and T denote diffusion coefficient, viscosity, and temperature, respectively) for Sb(III) remains constant over the entire range of basic-melt composition.⁹ However, it differs by 300% from the respective, but also constant, value characteristic of Sb(III) in the acidic melt. This indicates that there is only one species dominant in both basic and acidic melts and that they differ. Also, the entire change of the structure of the complex occurs in the proximity of a "neutral" melt.

Another feature of the Sb(III)/Sb system that changes drastically on going from basic to acidic melts is the reduction potential; Sb(III) reduction in basic melts occurs over 1 V more negative than in acidic melts. The comparison of these processes in basic and acidic melts is presented in Figure 1.

To study the behavior of the Sb(III) species in a neutral, unbuffered melt, the following procedure was employed. A solution of SbCl_3 in an exactly neutral $\text{AlCl}_3\text{-ImCl}$ melt was prepared. The cyclic voltammogram and rotating disk electrode (RDE) voltammogram curves for this solution are presented in Figure 2. The heights of both RDE reduction waves are proportional to the SbCl_3 concentration; however, they do not follow the Levich equation dependence on $\omega^{1/2}$ for convective-diffusion-controlled

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