Inorg. Chem. **1982**, *21*, 4197–4204

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Complexes and Cations Supported on the Surface and between the Layers of Zirconium Phosphate. 1. Copper(II) and Its Ammonia Complexes[1]

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Received August 11, 1981

The nature of the Cu(II)–aquo and –ammine complexes which form on the surface of the layered inorganic ion exchanger α-zirconium phosphate, $Zr(HPO_4)_2\cdot H_2O$, has been examined by means of ESR and UV–visible reflectance spectra. At low surface coverage, the ESR spectra of both the highly crystalline and semicrystalline exchangers are mainly due to isolated hexaaquocopper ions. However, resonances due to nonlinear pairs and species that yield reversed *g* parameters ($g_\perp > g_\parallel$) are also observed. As the loading increases, the concentration of nonlinear pairs increases proportionately until finally at ~20% coverage only this species is obtained. The copper complexes are octahedral with tetragonal distortion. In the amorphous form of the exchanger the Cu(II) species are free to tumble much as in aqueous solution. When the protons were exchanged out with Na^+, nonlinear Cu(II) pairs were not observed even up to 25% coverage of the surface by Cu(II). On dehydration, diffusion of copper ions into the interior takes place with an accompanying change of symmetry to trigonal. Sorption of NH_3 by Cu(II) on hydrated zirconium phosphate results in formation of $[Cu(NH_3)_5H_2O]^{2+}$. However, in the dehydrated state the tetraammine complex forms. Explanations for the observed behavior are given on the basis of the known structure of the host lattice.

Introduction

The heterogenization of homogeneous catalysts is an area of intense current interest.[3a,b] Complexes have been affixed to polymers,[3a,c] formed in zeolite cavities,[4,5] and affixed to silica or alumina surfaces.[6] Recently bulky complexes have been incorporated between the layers of a smectite clay, hectorite, by an ion-exchange process, and these products have exhibited interesting catalytic behavior.[7,8]

The ion-exchange method of catalyst immobilization on layered compounds is simple when compared to the procedures required for attachment of complexes to polymers. The attractiveness of the method is further increased by providing temperature- and solvent-stable inorganic layered exchangers of known structure as supports. The group 4B phosphates form layered compounds of two types: those with a relatively small interlayer spacing (7.6 Å), the so-called α type, and another with a larger interlayer spacing (~12 Å), or γ type.[9] α-Zirconium phosphate, $Zr(HPO_4)_2\cdot H_2O$, abbreviated α-ZrP, is the best known of the group. Its ion-exchange properties have been examined in detail,[9-11] and in the hydrogen form it is known to be an acidic catalyst.[12,13] Thus it was of interest to determine whether catalytically active complexes could be immobilized on these layered compounds. We are particularly interested in oxygen carriers in which Co(II) or Cu(II) interacts with molecular oxygen. In this paper we discuss the exchange behavior of Cu(II)–aquo and –ammine complexes with α-ZrP.

α-ZrP can be prepared as an amorphous gel, as crystals, and in intermediate states of crystallinity.[14,15] The surface area increases as the crystallinity decreases.[16] Surface areas of greater than 200 m^2/g are possible by control of the conditions of preparation. In such samples a large proportion of the exchange sites reside on the surface, and complexes fixed to such surfaces may be present in sufficient amount to effect macroscopic catalytic transformations. However, it is almost certain that the surfaces of the less crystalline samples differ in important respects from the highly crystalline surfaces. We therefore chose to probe these differences by examining complexes on the surface and between the layers of three samples of α-ZrP of widely differing crystallinities. A preliminary report on the incorporation of $[Cu(NH_3)_4]^{2+}$ in highly crystalline α-ZrP was given earlier.[17]

Experimental Section

Preparation of Exchangers. Three samples of zirconium phosphate were prepared as described previously[14,15] and labeled $\overline{HH}\cdot H_2O(0.5:48)$, $\overline{HH}\cdot H_2O(2.5:48)$, and $\overline{HH}\cdot H_2O(12:336)$. This designation means that the zirconium phosphate gel was refluxed in 0.5 M H_3PO_4 for 48 h etc. The barred species represent the exchangeable cations within the interlayer. The first sample is amorphous, the second semicrystalline, and the third highly crystalline. Surface areas were determined by ion exchanging the surface protons with ammonium ions.[16] Surface areas calculated with the assumption that each proton requires 24 $Å^2$ of the surface were as follows: $\overline{HH}\cdot H_2O(0.5:48)$, 180 m^2/g; $\overline{HH}\cdot H_2O(2.5:48)$, 75 m^2/g; $\overline{HH}\cdot H_2O(12:336)$, 2.9 m^2/g. The fully exchanged sodium ion phase $\overline{NaNa}\cdot 3H_2O(2.5:48)$, i.e., $Zr(NaPO_4)_2\cdot 3H_2O$, was prepared as described previously.[18] These samples were characterized by TGA and X-ray powder diffraction patterns.

Surface Exchange of $\overline{HH}\cdot H_2O(2.5:48)$ and $\overline{NaNa}\cdot 3H_2O(2.5:48)$ with Cu(II). A stock solution of copper(II) acetate (0.1 N) was prepared by dissolving a weighed amount of solid and diluting with distilled deionized water to 1000 mL. Aliquots of this solution representing 24%, 48%, and 96%, respectively, of the surface exchange capacity (0.52 mequiv) were added to accurately weighted samples (1 g) of $\overline{HH}\cdot H_2O(2.5:48)$ and $\overline{NaNa}\cdot 3H_2O(2.2:48)$ with sufficient distilled deionized water to make the volume to solid ratio 100 mL/g. The mixtures were swirled for about 10–20 s each and quickly filtered.

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[1] This work was supported by a grant (CHE-79-16160) from the National Science Foundation for which grateful acknowledgment is made.

[2] This work formed a portion of the Ph.D. dissertation of L.R.Q., Texas A&M University, Aug 1981.

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Table I. Copper Analysis of $[Cu(H_2O)_6]^{2+}$ Surface-Exchanged Zirconium Phosphates

exchanger	amt of Cu, mequiv/g added	amt of Cu, mequiv/g found[a]	designation
$\overline{\text{HH}}\cdot H_2O(2.5:48)$	0.010	0.010	$Cu_{0.010}/_{s}\overline{\text{HH}}\cdot H_2O(2.5:48)$
$\overline{\text{HH}}\cdot H_2O(2.5:48)$	0.030	0.020	$Cu_{0.020}/_{s}\overline{\text{HH}}\cdot H_2O(2.5:48)$
$\overline{\text{HH}}\cdot H_2O(2.5:48)$	0.070	0.023	$Cu_{0.023}/_{s}\overline{\text{HH}}\cdot H_2O(2.5:48)$
$\overline{\text{HH}}\cdot 2H_2O(0.5:48)$	0.01	0.01	$Cu_{0.01}/_{s}\overline{\text{HH}}\cdot 2H_2O(0.5:48)$
$\overline{\text{HH}}\cdot 2H_2O(0.5:48)$	0.10	0.15	$Cu_{0.15}/_{s}\overline{\text{HH}}\cdot 2H_2O(0.5:48)$
$\overline{\text{HH}}\cdot 2H_2O(0.5:48)$	0.50	0.55	$Cu_{0.55}/_{s}\overline{\text{HH}}\cdot 2H_2O(0.5:48)$
$\overline{\text{HH}}\cdot H_2O(12:336)$	0.01	0.01	$Cu_{0.01}/_{s}\overline{\text{HH}}\cdot H_2O(12:336)$
$\overline{\text{HH}}\cdot H_2O(2.5:48)$	0.13	0.11	$Cu_{0.11}/_{s}\overline{\text{HH}}\cdot H_2O(2.5:48)$
$\overline{\text{HH}}\cdot H_2O(2.5:48)$	0.25	0.25	$Cu_{0.25}/_{s}\overline{\text{HH}}\cdot H_2O(2.5:48)$
$\overline{\text{HH}}\cdot H_2O(2.5:48)$	0.50	0.58	$Cu_{0.58}/_{s}\overline{\text{HH}}\cdot H_2O(2.5:48)$
$\overline{\text{NaNa}}\cdot 3H_2O(2.5:48)$	0.13	0.13	$Cu_{0.13}/_{s}\overline{\text{NaNa}}\cdot 3H_2O(2.5:48)$
$\overline{\text{NaNa}}\cdot 3H_2O(2.5:48)$	0.25	0.26	$Cu_{0.26}/_{s}\overline{\text{NaNa}}\cdot 3H_2O(2.5:48)$
$\overline{\text{NaNa}}\cdot 3H_2O(2.5:48)$	0.50	0.54	$Cu_{0.54}/_{s}\overline{\text{NaNa}}\cdot 3H_2O(2.5:48)$

[a] Neutron activation analysis.

The solid samples were then washed, dried in air, and stored in a desiccator over $CaSO_4$.

A stock solution of 0.01 N copper sulfate solution was prepared by dissolving a weighted amount of solid in distilled deionized water and diluting to 100 mL. Aliquots of this solution representing 1.9, 5.8, and 12.8% of the surface exchange capacity (0.52 mequiv) were added to 0.2500-g samples of $\overline{\text{HH}}\cdot H_2O(2.5:48)$ with sufficient distilled deionized water to make the volume to solid ratio 100 mL/g. The mixture was swirled for approximately 10–20 s and filtered. The samples were washed, air-dried, and stored in a desiccator over $CaSO_4$. The notation $Cu_{0.1}/_{s}\overline{\text{HH}}\cdot H_2O(2.5:48)$ will be used to describe surface exchanged samples where $Cu_{0.1}/_{s}$ represents 0.1 mequiv of copper exchanged onto the surface of the exchanger.

Surface Exchange of $\overline{\text{HH}}\cdot H_2O(12:336)$ and $\overline{\text{HH}}\cdot H_2O(0.5:48)$ with Cu(II). A stock solution of copper(II) acetate (0.001 N) was prepared by diluting 1 mL of the 0.1 mL solution to 100 mL. Aliquots of this solution representing 0.01, 0.05, and 0.5 mequiv were added to accurately weighted samples (~1 g) of $\overline{\text{HH}}\cdot H_2O(0.5:48)$. An aliquot of this solution, representing 0.01 mequiv, was also added to 1 g of $\overline{\text{HH}}\cdot H_2O(12:336)$. Each mixture was swirled for aobut 10–20 s and quickly filtered. The samples were washed, dried in air, and stored in a desiccator over $CaSO_4$.

Ammonia Adsorption. Ammonia adsorption was carried out with both hydrated and dehydrated surface Cu(II) exchanged samples of $\overline{\text{HH}}\cdot H_2O(2.5:48)$ and $\overline{\text{NaNa}}\cdot 3H_2O(2.5:48)$. The samples were dehydrated at 392 °C for 68 h in air. Approximately 0.25 g of the powdered samples was transferred to a vacuum sample tube. Each sample was first outgassed at room temperature at a pressure of $\sim 10^{-5}$ torr for 0.5 h. Adsorption of ammonia was carried out at room temperature in the vacuum system. Anhydrous tank ammonia (Linde Division, Union Carbide) was used without further purification. The NH_3 was admitted to the sample in doses of 1.0 mmol of NH_3 until no more was taken up. The solids was allowed to sit in excess NH_3 for 24 h. Spectroscopic measurements (ESR, UV–visible) were obtained without transfer of the samples. The solids were subsequently degassed in vacuo at room temperature overnight. Next, they were heated in vacuo at 100 °C for 1 h and finally at 200 °C for 1 h.

Instrumental Work

ESR spectra were recorded with the samples at −196 °C and room temperature by using a Varian E-6S spectrometer with a TE_{102} mode cavity. The g values were reported relative to a 2,2-diphenyl-1-picrylhydrazil (dpph) standard with $g = 2.0036$. A Cahn Electrobalance was used for the thermogravimetric analysis. A Cary 14 spectrometer with a type-II diffuse-reflectance attachment was used to obtain electronic spectra in the visible and near-infrared regions against MgO as reference. X-ray powder diffraction patterns were obtained by using a Siefert Scintag Automated Powder Diffraction Unit (PAD II) with Cu K_α radiation. The solids were analyzed for C, N, and H by the Center for Trace Characterization at Texas A&M. Copper and zirconium were determined by the neutron activation analysis method reported by Clearfield and Day.[19]

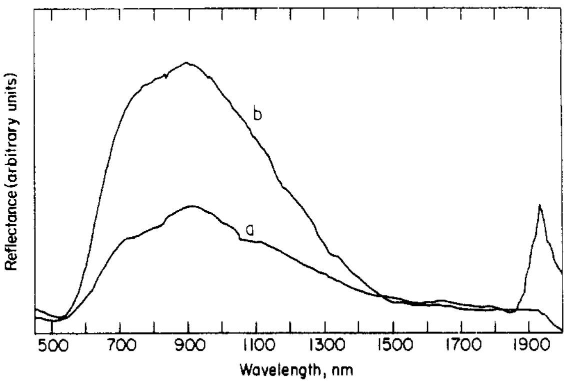

Figure 1. Reflectance spectra of Cu^{2+}-exchanged $\overline{\text{HH}}\cdot H_2O(2.5:48)$: (a) surface $[Cu(H_2O)_6]^{2+}$ species; (b) complex dehydrated at 392 °C.

Results

Copper(II)–Aquo Complexes. The analytical data for the determination of Cu(II) on the solid samples are shown in Table I. When $Cu(OAc)_2\cdot H_2O$ was used in the exchange reaction, quantitative uptake of Cu(II) was found to occur. However, with $CuSO_4\cdot 5H_2O$, extremely small quantities of Cu(II) were taken up by the support. This results is a consequence of the pH difference in the two solutions, 5.8 for the former and 3.4 for the latter. Much less Cu(II) is exchanged in an acidic solution because the exchange reaction, expressed in eq 1, is shifted toward the left.[20]

$$Cu^{2+} + HH/_{s}\overline{\text{HH}}\cdot H_2O \rightleftarrows Cu/_{s}\overline{\text{HH}}\cdot H_2O + 2H^+ \quad (1)$$

The reflectance spectrum of $[Cu(H_2O)_6]^{2+}$ exchanged onto the surface of $\overline{\text{HH}}\cdot H_2O(2.5:48)$ is shown in Figure 1a. The spectrum has a maximum absorbance at 760 nm and another at 900 nm and is asymmetric toward the low-frequency side. These band positions are virtually identical with those reported for $\overline{\text{Cu}}\cdot 4H_2O(12:336)$, where the Cu(II) is located between the layers.[21,22] However, the intensities are different. Buckley[22] obtained nearly equal peak heights for the maxima using 12:336 as the exchanger while Allulli et al.[21] did not observe the peak at 900 nm. These differences indicate that more than one species is present on the surface. The peak at 760 nm has been interpreted as representing Cu(II) in a tetragonally distorted octahedral environment. This interpretation is based on comparison between tetragonality and band position.[21] The observed band positions compare extremely well with those reported for $Cu(H_2O)_4(HCO_2)_2$.[23] By analogy, we ascribe the structure of the major surface-exchanged Cu(II)–aquo complex to be that of a tetragonally distorted octahedron.

The ESR spectra of $[Cu(H_2O)_6]^{2+}$ exchanged on to the surface of $\overline{\text{HH}}\cdot H_2O(2.5:48)$ are shown in Figure 2. The spectra for the randomly oriented powder samples at −196 °C consist of resonances that can define Cu(II) species. The parameters $g_\parallel = 2.38$, $g_\perp = 2.06$, and $|A_\parallel| = 130$ G represent an isolated species with axial symmetry. This corresponds to the hexaaquocopper(II) complex,[24,25] which is probably distorted by a tetragonal elongation, as shown in the reflectance spectrum. The band at $g_\parallel = 2.28$ is attributed to nonlinear pairs of Cu(II) ions coupled together by exchange interac-

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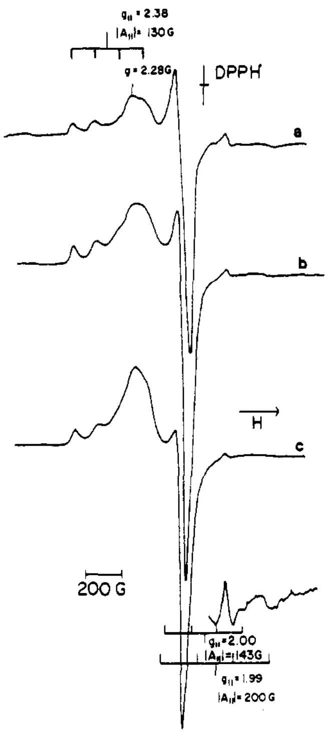

Figure 2. ESR spectra of Cu(II)–aquo species on the surface of $\overline{\mathrm{HH}}\cdot\mathrm{H_2O}(2.5{:}48)$: (a) 0.010 mequiv; (b) 0.020 mequiv; (c) 0.023 mequiv.

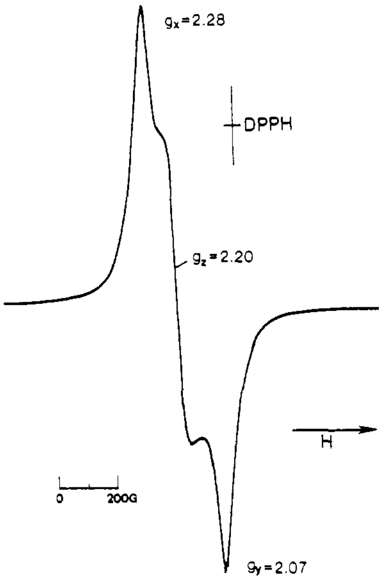

Figure 3. ESR spectrum of $\mathrm{Cu_{0.11}/_s\overline{HH}\cdot H_2O(2.5{:}48)}$.

tions.[26] The spectrum of the nonlinear pair consists of two parts: one symmetric main line and one much weaker half-field line. As the concentration of surface copper is increased, the spectrum of the nonlinear pairs grows until at 0.1 mequiv/g of exchanger (19% of the surface capacity) the spectrum is that of only the nonlinear Cu(II) ion pairs (Figure 3).[27] The spectra (Figure 2) also indicate the presence of two species with reversed ESR parameters ($g_\perp > g_\parallel$), $g_\parallel = 1.99$, $|A_\parallel| = 200$ G and $g_\parallel = 2.00$, $|A_\parallel| = 143$ G. The spectra of these species constitute much less intense portions of the spectrum. Possible explanations for the reversed *g* values will be presented in the Discussion.

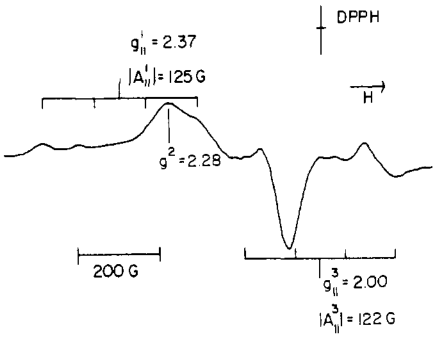

Figure 4. ESR spectrum of $\mathrm{Cu_{0.01}/_s\overline{HH}\cdot H_2O(12{:}336)}$.

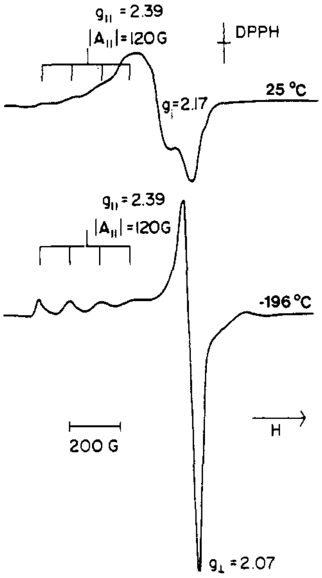

Figure 5. ESR spectra of $\mathrm{Cu_{0.01}/_s\overline{HH}\cdot 2H_2O(0.5{:}48)}$.

The ESR spectrum of $\mathrm{Cu_{0.01}/_s\overline{HH}\cdot H_2O(12{:}336)}$ (Figure 4) is very similar to that observed when $[\mathrm{Cu(H_2O)_6}]^{2+}$ is exchanged onto the surface of $\mathrm{\overline{HH}/_s\cdot H_2O(2.5{:}48)}$ in quantities of less than 0.10 mequiv/g of exchanger. Three distinct Cu(II) species are observed. One is attributed to isolated $[\mathrm{Cu(H_2O)_6}]^{2+}$ ions with $g_\parallel = 2.37$, $g_\perp = 2.06$, and $|A_\parallel| = 120$ G and an isotropic signal with $g_\mathrm{i} = 2.17$, as determined by the crossing of the base line. At −196 °C the spectrum consists of clearly defined $g_\parallel$ and $g_\perp$ components, as expected for an isolated Cu(II) with axial symmetry with $g_\parallel = 2.39$, $g_\perp = 2.07$, and $|A_\parallel| = 120$ G. The ESR spectra of 0.10 mequiv of Cu(II) on the exchanger at room temperature and at −196 °C are similar to those observed with 0.01 mequiv Cu(II). When the concentration of Cu(II) is increased to 0.55 mequiv, the room-temperature spectrum consists of an isotropic signal with $g_\mathrm{i} = 2.17$, while the spectrum at −196 °C contains both the isotropic signal and the anisotropic spectrum, due to isolated Cu(II) ions. The spectra at −196 °C show variations in the line widths of the parallel hyperfine lines. In addition, the ESR spectral parameters for the isolated Cu(II) species with axial symmetry are somewhat larger than those found for the $[\mathrm{Cu(H_2O)_6}]^{2+}$ exchanged on $\mathrm{\overline{HH}\cdot H_2O(12{:}336)}$, on $\mathrm{\overline{HH}\cdot H_2O(2.5{:}48)}$, and in zeolites.[27] However, the calculated average values of *g* ($g_\mathrm{av} = {}^1/_3 g_\parallel + {}^2/_3 g_\perp$) are in good agreement with the observed values of g_av for Cu(II) in aqueous solution.[28]

The ESR results, together with the fact that more water occupies the interlamellar region in the gel than in the crystals,[9,15] suggest that some Cu(II) species, at room temperature,

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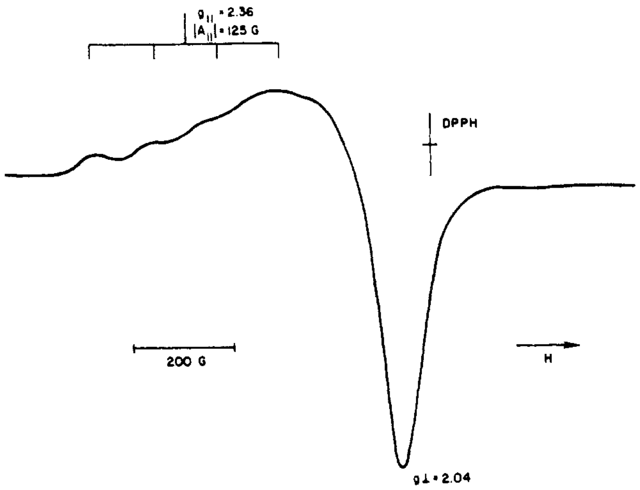

Figure 6. ESR spectrum of $Cu_{0.13}/{}_s\overline{NaNa}\cdot 3H_2O(2.5{:}48)$.

Table II. Electron Spin Resonance Parameters for Cu(II)-Aquo Species on the Surface of Zirconium Phosphates

	isolated $[Cu(H_2O)_6]^{2+}$		pairs of Cu(II)-aquo ions	reversed spectra		
exchanger	$g_{\parallel}$	$\lvert A_{\parallel}\rvert$, G	g	$g_{\parallel}$	$\lvert A_{\parallel}\rvert$, G	$g_{\perp}$
$\overline{HH}\cdot H_2O(2.5{:}48)$	2.38	130	2.28[a]	1.99 2.00	200 143	2.06
$\overline{HH}\cdot H_2O(12{:}336)$	2.37	125	2.28[a]	2.00	122	2.06
$\overline{HH}\cdot 2H_2O(0.5{:}48)$	2.39	120	2.17[b]			2.07
$\overline{NaNa}\cdot 3H_2O(2.5{:}48)$	2.36	125				2.04

[a] g value at signal maximum. [b] g value at crossing of the base line.

are tumbling in a solution-like environment, whereas others occupy sites in which this motion is restricted. Rapid intramolecular exchange can occur between three equivalent Jahn-Teller distorted states, which correspond to axial elongation along the three sites of water-copper-water axis.[29] However, when the ion is adsorbed on a surface, this motion will not lead to averaging of $g_{\parallel}$ and $g_{\perp}$ in the absence of rapid tumbling.

The aquocopper(II) ion was also exchanged onto the surface of $\overline{NaNa}\cdot 3H_2O(2.5{:}48)$. Figure 6 shows the ESR spectrum of a sample in which 0.13 mequiv of $[Cu(H_2O)_6]^{2+}$ was exchanged onto the surface. It is characterized by $g_{\parallel} = 2.36$, $g_{\perp} = 2.04$, and $|A_{\parallel}| = 125$ G. At higher copper-exchange levels spin-exchange interactions between the paramagnetic ions, which result in the appearance of the isotropic spectrum (Figure 3) when $\overline{HH}\cdot H_2O(2.5{:}48)$ is the support, are not observed, even at total surface coverage. It seems that the mechanism for paramagnetic exchange depends on the nature of the support. The g values are characteristic of the $[Cu(H_2O)_6]^{2+}$ ion.[24,25] Table II summarizes the ESR parameters for the copper-aquo species.

Dehydrated Samples. The surface-exchanged samples were dehydrated by heating in air at 392 °C for 62 h. In the case of the crystalline phase $ZrCu(PO_4)_2\cdot 4H_2O$, this treatment is sufficient to remove all of the water,[21,30] and in the process the interlayer distance is reduced from 9.4 to 7.8 Å. However, both the ESR and the UV-visible spectra remain essentially unchanged. In contrast, our surface-exchanged α-ZrP samples retain the structure of the original hydrogen form of α-ZrP. On dehydration α-ZrP is transformed into ζ-ZrP (7.41-Å interlayer spacing) at slightly above 100 °C and to η-ZrP at about 230 °C.[31] The latter phase change is reversible so that the ζ phase is obtained upon cooling the dehydrated samples.

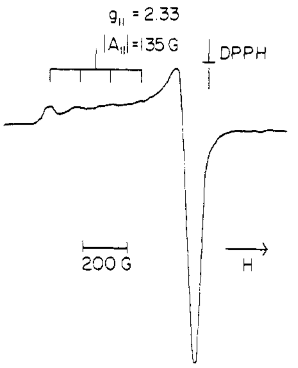

Figure 7. ESR spectrum of anhydrous $Cu_{0.11}/{}_s\overline{HH}(2.5{:}48)$.

The ESR spectra of the dehydrated 2.5:48 samples, shown in Figure 7, were similar irrespective of loading (0.1-0.5 mequiv/g). The low-field portions of the spectra were poorly resolved as only one set of parameters ($g_{\parallel} = 2.33$ and $|A_{\parallel}| = 135$ G) could be identified in each of the samples. Dehydration of the Cu(II) surface-exchanged $\overline{NaNa}\cdot 3H_2O$ samples (loadings of 0.13-0.54 mequiv/g Cu^{2+}) resulted in ESR spectra in which the parallel hyperfine lines could not be resolved at all. In addition, a decrease in the intensity of the ESR signals was observed for all of the dehydrated samples. One possible explanation for the observed loss of intensity is that reduction of Cu(II) to Cu(I) may have occurred.[32] Since the dehydration was carried out in air, reduction is unlikely. It is feasible to consider that some of the Cu(II) ions are located in a site such as one with trigonal-planar symmetry that would result in an orbitally degenerate ground state. In such an instance the ESR absorption would not be detected.[33]

A change occurred in the absorption spectrum of Cu(II)-exchanged samples of $\overline{HH}(2.5{:}48)$ on dehydration (Figure 1b). The band at 900 nm is unchanged, the shoulder at 1055 nm disappeared, and the band at 760 nm shifted to ~810 nm. This spectrum resembles that reported for dehydrated $\overline{Cu}\cdot 4H_2O(12.336)$,[21,22] which has bands at 714 and 800 nm. We interpret these results as indicating diffusion of the surface Cu(II) ions into the interior. However, we give a different interpretation to the coordination of the dehydrated Cu(II) species. As has been mentioned earlier, the symmetry of both the hydrated and dehydrated Cu(II) in the interlayer was assigned as distorted tetragonal octahedral.[21,22] Examination of the zirconium phosphate structure reveals no position where a Cu(II) could be coordinated to four lattice oxygens in a planar arrangement at distances of ~2.0 Å and two trans oxygens at 2.2-2.55 Å. From consideration of the ESR data the sterochemistry of the Cu(II) could be tetragonally elongated octahedral, square planar, square pyramidal, tetrahedral, or distorted trigonal.[34] The same structual argument used above to rule out the tetragonal stereochemistry can be applied to the square-planar and square-pyramidal geometries. In addition, Cu(II) in these environments would have a much higher $|A_{\parallel}|$ value than actually observed.[27] Square-planar and square-pyramidal complexes are known to give visible absorptions at frequencies in the range 500-650 nm.[34] Complexes with tetrahedral geometry would give d-d transitions at much higher wavelengths as, for example, that for the dodecatungstocuprate(II) anion, which occurs at 1430 nm.[35]

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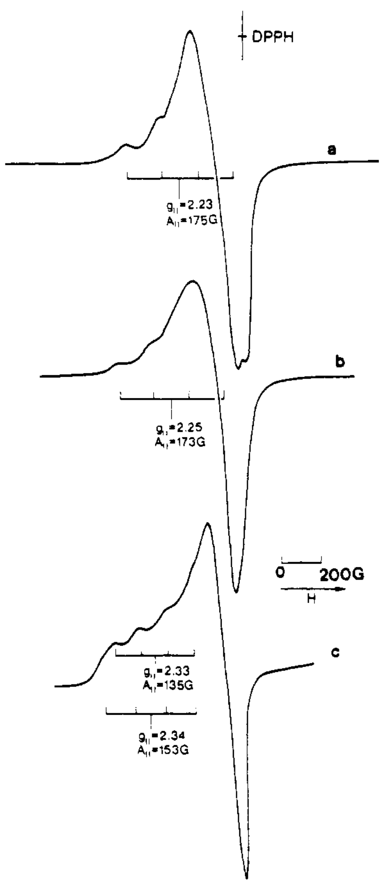

Figure 8. ESR spectra of the Cu(II) species on $\overline{HH}$(2.5:48): (a) after ammonia adsorption; (b) after evacuation overnight at 25 °C; (c) after evacuation 1 h at 100 °C.

The reflectance spectrum for Cu(II) in Y-type zeolites, which is thought to be coordinated to three lattice oxygens (C_{3v}), has bands at 820 and 950 nm.[36] The similarity of the observed frequencies for Cu(II) in zeolites with our data would suggest that the symmetry of the Cu(II) in these zirconium phosphate samples after dehydration is also trigonal. This will be elaborated upon in the Discussion.

The reflectance spectrum of surface $[Cu(H_2O)_6]^{2+}$ on $\overline{NaNa}\cdot 3H_2O$(2.5:48) is slightly different from the spectrum when $\overline{HH}\cdot H_2O$(2.5:48) is the support. The shoulder at ~810 nm is more intense, the band at 900 is unchanged, and there is now a shoulder at ~1055 nm.

Adsorption of Ammonia. Exposure of α-ZrP to either gaseous or dissolved ammonia results in its being intercalated until each proton site is ammoniated.[37] Therefore, the amount of NH_3 sorbed by copper(II) ions loaded in α-ZrP could not be determined by pressure changes. However, the presence of copper-ammine complexes was revealed by ESR and visible spectroscopy.

The three dehydrated samples of $\overline{HH}$(2.5:48) surface-exchanged solids containing 0.13, 0.25, and 0.58 mequiv/g of Cu^{2+} were exposed to gaseous NH_3 at about 450 torr in a sealed tube. Approximately 120 h was required for the reaction to be complete, probably owing to the slow intercalation reaction. This is in contrast to the much more rapid uptake with hydrated samples. The ESR spectra of the resultant products were identical (Figure 8a) and due to isolated anisotropically oriented copper–ammonia complexes ($g_{\parallel} = 2.23$, $g_{\perp} = 2.04$, and $|A_{\parallel}| = 175$ G). It should be remembered that the host lattice is now in the ammonium ion form, $Zr(NH_4PO_4)_2$ with an interlayer distance of 9.38 Å.[38] The observed parameters are in agreement with those reported for $[Cu(NH_3)_4]^{2+}$ in other supports.[39-44] By analogy, we conclude that the copper–ammine complex in α-ZrP is either square planar or octahedral with tetragonal elongation. Evacuation overnight at room temperature produced no significant change in the ESR spectra (Figure 8b).

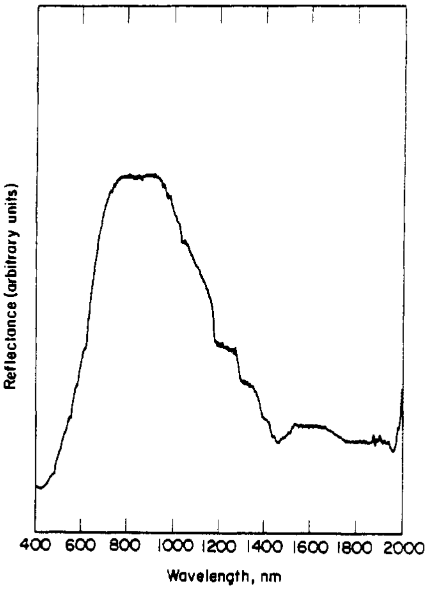

Figure 9. Reflectance spectrum of the Cu(II)–ammonia complex on anhydrous $\overline{HH}$(2.5:48).

Addition of excess gaseous ammonia to the anhydrous sodium ion phase 2.5:48 containing 0.13–0.54 mequiv of Cu(II) yielded ESR spectra with $g_{\parallel} = 2.25$ and $g_{\perp} = 2.05$ and a hyperfine splitting constant of $|A_{\parallel}| = 220$ G. These values are similar to those cited for copper ion in the complex $[Cu(NH_3)_4][PtCl_4]$.[45] The large difference in the hyperfine splitting constants (NH_4^+ vs. Na^+ phases) indicates that the nature of the counterion has a dramatic effect on the environment of the Cu(II). This is in contrast to what is observed in zeolites.[41]

Evacuation of the ammonia-treated sodium ion phases at room temperature overnight resulted in the appearance of a second set of parameters with $g_{\parallel} = 2.32$ and $|A_{\parallel}| = 135$ G, which is attributed to a dehydrated Cu(II) species. Apparently desorption of ammonia from the complex occurs more readily when the support is $\overline{NaNa}$(2.5:48).

The reflectance spectrum of the copper–ammonia complex formed on $\overline{HH}$(2.5:48) by NH_3 sorption is shown in Figure 9. This spectrum exhibits two bands of equal intensities at 800 and 900 nm and a weak shoulder at ~1040 nm. The spectrum of the complex on $\overline{NaNa}$(2.5:48) has a very broad absorption, whose maximum is at 900 nm, and a band at 800 nm which is not as intense as in the $\overline{NH_4NH_4}$ phase. Also, the shoulder at 1050 nm is extremely weak. These spectra do not resemble the optical spectra of the square-planar $[Cu(NH_3)_4]^{2+}$ complex in solution or after its exchange within

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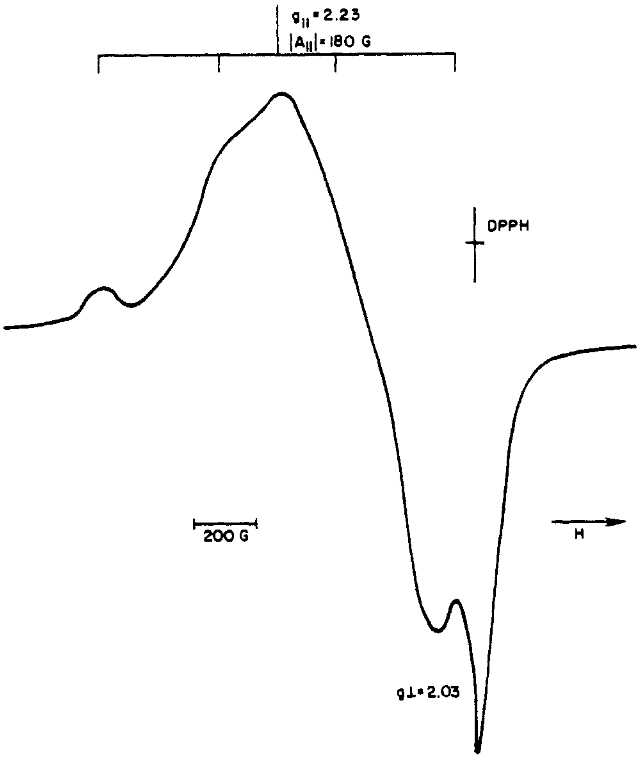

Figure 10. ESR spectrum of the Cu(II)-ammonia complex on the surface of $\overline{\mathrm{HH}}\cdot\mathrm{H_2O}$(2.5:48).

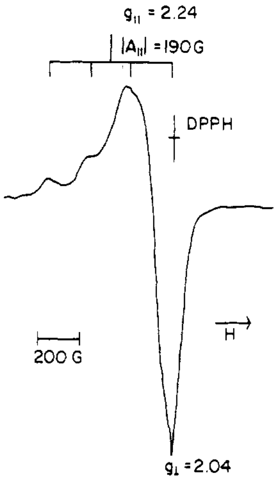

Figure 11. ESR spectrum of the Cu(II)-ammonia complex on the surface of $\overline{\mathrm{NaNa}}\cdot 3\mathrm{H_2O}$(2.5:48).

the layers from solution.[46] However, the observed absorption bands are characteristic of copper complexes which are tetragonal such as the spectra of the copper(II)-aquo complexes discussed previously.

Different results were obtained when the concentration of surface Cu(II) was very low. For example, ammonia adsorption on $\mathrm{Cu_{0.01}/_s\overline{HH}\cdot H_2O(2.5{:}48)}$ and $\mathrm{Cu_{0.13}/_s\overline{NaNa}\cdot 3H_2O(2.5{:}48)}$ resulted in the formation of a copper-ammonia complex on both supports as indicated in the ESR spectra shown in Figure 10 and 11, respectively. The paramagnetic parameters for the complex formed on $\mathrm{Cu_{0.01}/_s\overline{HH}\cdot H_2O}$-(2.5:48) are $g_\parallel = 2.23$, $g_\perp = 2.04$, and $|A_\parallel| = 180$ G, whereas those on $\mathrm{Cu_{0.13}/_s\overline{NaNa}\cdot 3H_2O(2.5{:}48)}$ are $g_\parallel = 2.24$, $g_\perp = 2.03$, and $|A_\parallel| = 190$ G. These latter values are very similar to those reported for $[\mathrm{Cu(NH_3)_5}]^{2+}$ both in a frozen unadsorbed solution and on silica gels.[47,48] Evacuation at room temperature overnight produced no change in the ESR parameters. The reflectance spectra of the complex on both supports consist of a band with a maximum at 700 nm, which is in agreement with that of $[\mathrm{Cu(NH_3)_5H_2O}]^{2+}$ in aqueous solution (667 nm).[49]

Table III. Electron Spin Resonance Parameters for $\mathrm{Cu^{2+}}$-Exchanged Zirconium Phosphates under Various Conditions after Exposure to $\mathrm{NH_3}$

exchanger	$g_\parallel$	$\lvert A_\parallel\rvert$, G	$g_\perp$
After Ammonia Adsorption			
$\overline{\mathrm{HH}}$(2.5:48)	2.23	175	2.04
$\overline{\mathrm{NaNa}}$(2.5:48)	2.25	220	2.05
$\overline{\mathrm{HH}}\cdot\mathrm{H_2O}$(2.5:48)	2.23	180	2.04
$\overline{\mathrm{NaNa}}\cdot 3\mathrm{H_2O}$(2.5:48)	2.24	190	2.03
Following Evacuation at Room Temperature			
$\overline{\mathrm{HH}}$(2.5:48)	2.25	173	2.04
$\overline{\mathrm{NaNa}}$(2.5:48)	2.25	220	2.05
	2.32	135	2.05
Following Evacuation at 100 °C			
$\overline{\mathrm{HH}}$(2.5:48)	2.33	135	2.04
	2.34	153	2.04
$\overline{\mathrm{NaNa}}$(2.5:48)	2.32	135	2.04
	2.34	153	2.04

Desorption of Ammonia. The ammoniated dehydrated zirconium phosphate solids were degassed in vacuo at 100 °C overnight. Figure 8c shows that desorption of ammonia from the Cu(II) occurred. At least two distinct Cu(II) species were identified in each spectrum. The degassing of the $\overline{\mathrm{HH}}$(2.5:48) solids resulted in ESR spectra with $g_\parallel = 2.33$, $|A_\parallel| = 135$ G, $g_\parallel = 2.34$, $|A_\parallel| = 153$ G, and $g_\perp = 2.04$. The first set of parameters was also present in the ESR spectra obtained by dehydration of the surface-exchanged $[\mathrm{Cu(H_2O)_6}]^{2+}$ ion on α-ZrP(2.5:48) in air at 392 °C. Similarly, the $\overline{\mathrm{NaNa}}$(2.5:48) solids gave values for the Cu(II) species of $g_\parallel = 2.32$, $|A_\parallel| = 135$ G, $g_\parallel = 2.34$, $|A_\parallel| = 153$ G, and $g_\perp = 2.04$. These values are very similar to those found for dehydrated Cu(II) species in Y-type zeolites.[27] A summary of the ESR parameters is given in Table III.

Discussion

α-Zirconium phosphate, $\mathrm{Zr(HPO_4)_2\cdot H_2O}$, has a layered structured in which the metal atoms lie nearly in a plane and are bridged by phosphate groups.[50] Three oxygens of each phosphate group are bonded to three different zirconium atoms arranged at the apices of a nearby equilateral triangle. The fourth points away from the layer and bonds to a hydrogen atom. Adjacent layers are staggered in a pseudohexagonal fashion so as to form six-sided cavities between the layers. A water molecule sits in the center of each cavity. The layers are held together by van der Waals forces as there are no hydrogen bonds between the layers. The ion-exchange behavior of the less crystalline supports was interpreted on the basis of these solids having $\mathrm{PO_4}^{3-}$ groups shifted or tilted from their equilibrium positions in the crystal so as to provide cavities of different sizes.[9,15]

Copper-Aquo Complexes. The semicrystalline and crystalline α-ZrP supports appear to provide similar environments for Cu(II). The Cu(II) species are rigidly fixed at specific sites, and unlike the case of Cu(II) on the amorphous support, the effects of rapid tumbling at room temperature are not

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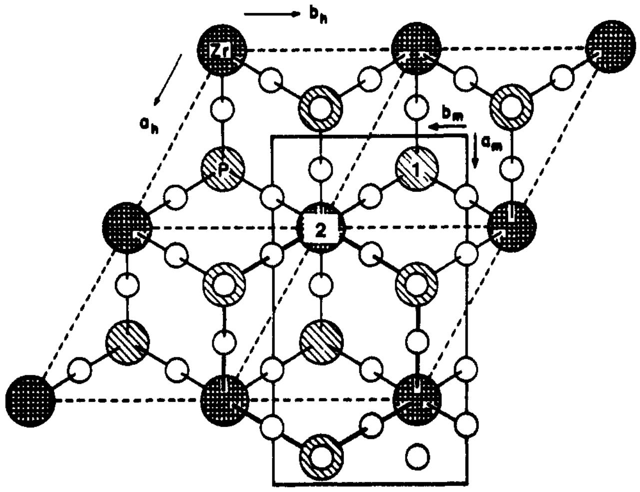

Figure 12. An idealized portion of a layer of α-zirconium phosphate.

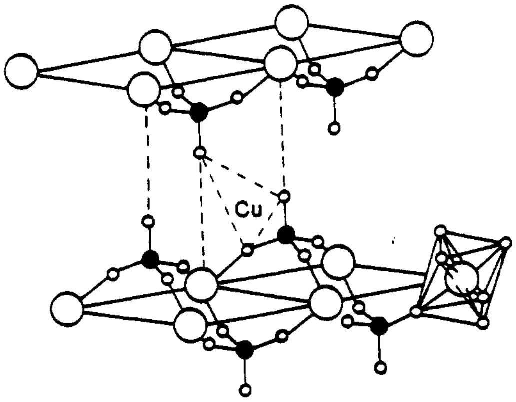

Figure 13. Relative position of Cu^{2+} in anhydrous zirconium phosphate showing trigonal coordination.

observed in the ESR. Low Cu(II) concentrations on both $\overline{\mathrm{HH}}\cdot H_2O$(2.5:48) and $\overline{\mathrm{HH}}\cdot H_2O$(12:336) give ESR spectra representing isolated $[Cu(H_2O)_6]^{2+}$, nonlinear pairs of Cu(II) ions, and species with reversed parameters ($g_\perp > g_\parallel$). Only one set of reversed g values was observed for Cu(II) on $\overline{\mathrm{HH}}\cdot H_2O$(12:336) whereas two sets of parameters were present in the spectra of the less crystalline $\overline{\mathrm{HH}}\cdot H_2O$(2.5:48) support. In the highly crystalline α-ZrP, as a first approximation, all the cavities may be considered to be identical. However, with 2.5:48 a range of cavity sizes exists.[9,15] Therefore, more than one type of site may be created in the semicrystalline solid that allows Cu(II) to assume a stereochemistry resulting in reversed g values. Cu(II) complexes will give a reversed spectrum ($g_\perp > g_\parallel$) if the geometry is one of the following: compressed tetragonal octahedral, compressed rhombic octahedral, trigonal bipyramidal, cis-distorted octahedral, or linear.[34,51] The unpaired electron in these configurations would be in the d_{z^2} orbital. Model studies with the half-layer (Figure 12) indicate that the two most probable configurations that could give rise to the reversed spectra are the cis-distorted octahedron and the compressed tetragonal octahedron. In the highly crystalline solid the distances between pairs of phosphate oxygens, which bear the exchangeable protons, are 5.3 and 5.9 Å. A cis-distorted stereochemistry would arise if one proton from each of two waters coordinated cis to Cu(II) were to form a hydrogen bond with each oxygen of a pair of $P-O^-$ groups at the surface. Hydrogen bonding in this manner to either pair of oxygens would cause the O–Cu–O angle to become less than 90° and to produce the same results as a chelating ligand with small bite. Likewise, a compressed tetragonal geometry could be envisioned if the two water molecules in the axial positions each hydrogen bond to an orthophosphate oxygen at the surface. This would shorten the Cu–O axial bond lengths, and a d_{z^2} ground state would result. However, model studies show that the resulting hydrogen bonds would be bent no matter whether the interaction occurred with the orthophosphate oxygens separated by 5.9 or 5.3 Å. Therefore, the cis-distorted-octahedral coordination is more likely.

The formation of nonlinear pairs of Cu(II) ions on the surface may rise when one Cu(II) becomes fixed in a half-cavity above a phosphate group, position 1, Figure 12, and another Cu(II) resides over an adjacent Zr, position 2, Figure 12. For electroneutrality to be maintained four protons must be lost. Each Cu(II) ion would be surrounded by three $P-O^-$ groups, but repulsion of the positive charges on the coppers may influence each to be closer to two $P-O^-$ groups than to the third. It is interesting that even at very low Cu(II) concentrations the signal due to nonlinear pairs is observed in the ESR spectra. One might instead expect the cations to be evenly distributed on the surface.

Some of the Cu(II) species on the amorphous support are in a solution-like environment and at room temperature are tumbling rapidly. The Cu(II) ions characterized by the anisotropic signal in the room-temperature spectrum occupy fixed sites. Because of the gel-like nature of 0.5:48, it is probable that its surface is more highly hydrated than that of the more crystalline samples. In addition, this amorphous zirconium phosphate has a wide distribution of cavity sizes. Thus, a Cu(II) ion in a larger than average surface cavity would be weakly bonded and behave as if in a solution-like environment. Similarly, a Cu(II) ion in a smaller than average cavity may be strongly bonded between a pair of $P-O^-$ groups that are closer together than 5.3 Å and become fixed. Similar situations would exist for Cu(II) ions in the interior of the exchanger.

The possibility always exists that some diffusion into the interior has occurred. Preliminary experiments with α-ZrP-(12:15), using 10 times the amount of Cu^{2+} required to cover the surface, revealed that an uptake equivalent to one-third of the surface capacity took place in 30 s and 60% in 6 min. Thus, it is unlikely that any significant diffusion into the interior occurred in 10–20 s with 12:336. Similar experiments with less crystalline samples are in progress, but the similarity of the spectra of 12:336 and 2.5:48 indicates that diffusion into the interior with the latter sample is also minimal.

Dehydrated species. There are several sites in the interlayer where a dehydrated Cu(II) would have a distorted trigonal environment. The Cu(II) could position itself between two phosphate oxygens that are situated alternatively above and below the planes of zirconium atoms. A lattice oxygen that does not bear a negative charge such as that shown in Figure 13 could be weakly coordinated to the Cu(II), thus providing the trigonal geometry. For zeolites in which the Cu(II) ion is thought to be localized in sites that provide a distorted trigonal environment, calculations reported by Klier et al.[52] indicate that the Cu(II) ion lies closer to two oxygens than the third. The unpaired electron is thought to reside in the $d_{x^2-y^2}$ or d_{xy} orbital. This would lead to a normal ESR spectrum ($g_\parallel > g_\perp$) of a Cu(II) ion with axial symmetry.

Ammonia Complexes. Dehydration of surface-exchanged Cu(II) zirconium phosphates followed by adsorption of ammonia leads to the formation of a $[Cu(NH_3)_4]^{2+}$ complex with tetragonal symmetry in the interlamellar region. Following dehydration the Cu(II) is situated very nearly between two

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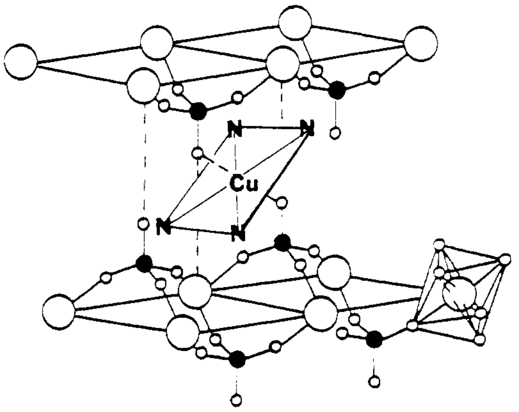

Figure 14. Relative position of the $[Cu(NH_3)_4]^{2+}$ complex in anhydrous zirconium phosphate.

phosphate oxygens that are situated alternatively above and below the planes of zirconium atoms. The different sites within a cavity are created by the different O–O interatomic distances. In $\overline{NH_4NH_4}$(2.5:48), the interlayer distance is 9.38 Å, and in $\overline{NaNa}$(2.5:48), it is 8.5 Å. This allows O–O distances of 5.17 and 4.65 Å in the former and 4.54 and 3.94 Å in $\overline{NaNa}$(2.5:48). In $\overline{NH_4NH_4}$(2.5:48), the O–O distance of 5.17 Å would result in a Cu–O bond length of 2.59 Å if a Cu^{2+} were directly between the two oxygens. This bond length is greater than values that are observed for the axial bond lengths in Cu^{2+} complexes with tetragonal coordination. However, the O–O distance of 4.65 Å would give a Cu–O bond length that is normal.[34] Therefore, in $\overline{NH_4NH_4}$(2.5:48) solids, the Cu^{2+} ion would preferentially situate itself between the pairs of oxygens separated by 4.65 Å, which corresponds to oxygens O_7–O_7'' and its equivalent positions.[50] In $\overline{NaNa}$(2.5:48), the O–O distance of 3.94 Å results in a Cu–O bond length that is slightly smaller than those that are unusually observed. The pairs of oxygens separated by 4.54 Å, which corresponds to oxygens O_{10}–O_7 and O_{10}'–O_7', results in a Cu–O bond length that is consistent with axial bond lengths in Cu^{2+} complexes with tetragonal coordination. The square-planar complex $[Cu(NH_3)_4]^{2+}$, which is approximately 5.5 Å across, could position itself between two $P–O^-$ groups that would then occupy trans axial positions. The plane of the $[Cu(NH_3)_4]^{2+}$ would be in an angle to the Zr layers as illustrated in Figure 14.

Adsorption of ammonia on zirconium phosphates that were not dehydrated resulted in surface ammonia complexes with five NH_3 groups coordinated to the metal. Unlike the ammonia of complexes formed in the interlayer region, a fifth NH_3 molecule would not be prevented from coordinating due to steric hindrance. Threfore it seems probable that a square-pyriamidal ammine complex forms on surfaces of both the $\overline{HH}\cdot H_2O$(2.5:48) and $\overline{NaNa}\cdot 3H_2$(2.5:48) supports rather than the square-planar tetrammine as in the interior.

Registry No. Cu, 7440-50-8; $Zr(HPO_4)_4\cdot H_2O$, 13933-56-7; $Cu(H_2O)_6^{2+}$, 14946-74-8; $Cu(NH_3)_5(H_2O)^{2+}$, 28998-54-1.

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Product Distribution and Stereochemistry in the Reaction of the Unsymmetrical Bis(phosphine) $Ph_2P(CH_2)_6P(Et)Ph$ with Platinum(II) Salts

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Received May 11, 1981

The new unsymmetrical bis(phosphine) $Ph_2P(CH_2)_6P(Et)Ph$ has been synthesized, and its reactions with platinum(II) salts have been studied. The formation of the cis or trans isomer with the ligand is critically dependent on the choice of the platinum(II) salt used as the starting material: potassium tetrachloroplatinate(II) yields the cis isomer, and Zeise's salt yields the trans isomer, while bis(benzonitrile)dichloroplatinum(II) gives a cis–trans mixture. The complexes are characterized by ^{31}P NMR and infrared spectroscopy, elemental analysis, and molecular weight data. The ^{31}P NMR spectrum of the trans complex is analyzed and explained in terms of the presence of different dimeric units present in solution. The new symmetrical bis(chiral phosphine) $Ph(Et)P(CH_2)_6P(Et)Ph$ and its platinum(II) complexes have been synthesized in order to confirm the spectral assignments. On the basis of the ^{31}P NMR spectra obtained, it is now possible to predict which unsymmetrical bis(phosphine)–platinum(II) complexes will give ^{31}P NMR spectra capable of complete analysis at 36.4-MHz field strength. The formation of the various isomers is also rationalized.

Introduction

There is much current interest in the synthesis and characterization of chelating bis(phosphine) ligands with chemically and magnetically different phosphorus nuclei attached to the same chelate backbone due to the utility of phosphorus-31 nuclear magnetic resonance as a probe for the investigation and elucidation of the factors that determine the stereochemistry and reactivity of the resulting transition-metal complexes. Symmetrical bis(tertiary phosphines) with flexible chelate backbones have been synthesized by a number of workers and their transition-metal complexes studied.[2-9] The

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