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Electron Paramagnetic Resonance Study of a Copper(II) Trimethylphosphine Oxide Complex in Y Zeolite

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Addition of trimethylphosphine to a rapidly dehydrated copper(II) Y zeolite resulted in the immediate reduction of the copper to the univalent oxidation state. After a brief evacuation, addition of oxygen caused the instantaneous oxidation of the Cu(I) ions and the complexing ligands. It is proposed that the resultant electron paramagnetic resonance (EPR) parameters of $g_\parallel = 2.44$, $A_\parallel = -87$ *Gauss, and* $g_\perp = 2.05$ *are due to tetrakis(trimethylphosphine oxide)copper(II) complexes located in the supercages of the Y zeolite lattice. By comparison to the EPR and bonding parameters of the aquo, ammine, and pyridine copper(II) analogs, it is suggested that this complex possesses pseudotetrahedral symmetry.*

Introduction

Natural and synthetic zeolites are increasingly being regarded as useful 'solvent' systems in which the rigid structural framework of the zeolites can stabilize transition metals in various oxidation states in particular coordination symmetries. In the dehydrated (activated) zeolites, the metal ions are often held in or near six-ring windows, with C_{3v} or D_{3h} symmetry respectively, in a manner such that trigonal coordination is maintained by three proximal lattice oxygen atoms. In addition, cations can be located in hexagonal prisms in synthetic X and Y zeolites and in faujasite where they are hexacoordinated by the lattice oxygens and, therefore, are rather shielded. Also of interest is the observation that in the more compact A zeolite, one of twelve large monovalent cations per unit cell can be forced into a "zero-coordinate' position [1]. Upon addition of various ligands to the activated transition metal-containing zeolites, complexes involving one to six ligand molecules can be formed. Some of these complexes have been characterized using electron paramagnetic resonance (EPR), optical, and crystallographic techniques, and the literature has been adequately summarized elsewhere [2–5].

No phosphine or phosphine oxide transition metal complex in zeolites has been previously reported, although it had been observed that an activated (Zn, K) A zeolite effectively sorbed trace amounts of PH_3 from SiH_4 preceding the preparation of silicon of semiconductor purity [6]. The formation of phosphine and phosphine oxide complexes in zeolites would be physically interesting because of the various cation locations in the different zeolites (structures of the zeolites have been compiled and discussed elsewhere [7, 8]), the sieving effect that would be observed due to the different diameters of the structural channels, and the option of varying the molecular size of the phosphine by altering the alkyl or aryl moieties on the phosphorus. The coordination numbers and copper oxidation state would have chemical implications, *e.g.* on the bond strengths of the complexes since copper(II) has stronger acid strength but weaker back-bonding than related copper(I) species. The resulting complexes would be of interest catalytically because at least some transition metal phosphines act as specific homogeneous catalysts, *e.g.* phosphine complexes of nickel carbonyls catalyze the cyclization of acetylene and its derivatives [9], and rhodium–phosphine complexes exhibit very high selectivity for the conversion of olefins to aldehydes [10]. In addition, it was observed that various copper(II) chelates coordinated to triphenylphosphine behave as effective initiators in the polymerization reaction of methyl methacrylate [11]. Recently, it has been found that molybdenum–dimethylphenylphosphine [12], nickel–tricyclohexylphosphine [13], and iridium–trimethylphosphine [14] complexes coordinate CO_2 where oxidation of the phosphine ligands does not occur and where these are potential catalysts for the fixation of CO_2 into organic compounds.

In the present study, Cu(II) was chosen as the transition metal ion to be investigated and Y zeolite was used as the matrix because Cu(II) Y zeolite has been thoroughly characterized by EPR [15]. It is well-known that divalent copper is readily reduced by tertiary phosphines to the univalent state. However, it was observed that the addition of triphenylphosphine to bis(acetylacetonato)copper(II) in chloroform resulted in a green solution in which no reduction of the cation occurred [16]. More recently the mono- and bis(triphenylphosphine) adducts of acetylacetonato [17], trifluoroacetylacetonato [18], and hexafluoroacetylacetonato [18, 19] copper(II) complexes have been isolated, and it was evident that the bidentate ligands stabilized the divalent copper in a square planar configuration. The present work was undertaken to determine by EPR the relative stabilities of the copper trimethylphosphine and trimethylphosphine oxide complexes in Y zeolite and to compare the resultant bonding and EPR parameters with those observed for other Cu(II) complexes held in the cavities of Y zeolite.

Experimental

Materials

A copper(II) exchanged Y zeolite was prepared by continuously stirring a Linde Na Y zeolite (Lot # 13544-76) in a filtered 0.01 *M* Cu(II) solution (volume/mass ratio = 20 cm^3/g) prepared from the nitrate salt. After equilibration for 4 hr at ambient temperature, the pH was found to be 7.0. The zeolite was then filtered, washed with 10 portions of water, and air-dried. The lattice-held copper(II) and sodium(I) concentrations were determined by atomic absorption following back-exchange with silver ion. The sum of the sodium ion (2.90 meq/g) and copper ion (0.32 meq/g) contents was equal to the ion exchange capacity of the zeolite (3.2 meq/g hydrated Y zeolite).

Oxygen was purchased from Air Reduction Co. and was used without further purification. The trimethylphosphine was procured from Strem Chemicals, Inc. Hydrogen, carbon monoxide, and ammonia were procured from Air Products and Chemicals, Inc. and used as received. Nitric oxide was obtained from Matheson Gas Products and was purified by repeatedly using the freeze–thaw technique with evacuation.

Formation of the Complexes

The zeolite was used in powder form and was degassed to 773 K under a dynamic vacuum in a conventional batch sample cell having a 4-mm o.d. quartz side arm that could be inserted into an EPR microwave cavity. The temperature was raised hourly in 100 K increments after first evacuating the cell for 1 hr at ambient temperature. After maintaining the final dehydration step for 1 hr, 250 Torr (1 Torr = 133.3 N/m^2) of O_2 was added and the temperature was held at 773 K for an additional 0.5 hr, at which time the cell was evacuated (10^{-4} Torr) for 0.08 hr. At room temperature, 300 Torr trimethylphosphine was added to the sample cell. After standing approximately 12 hr, the cell was evacuated for 15, 105, and 60 sec sequentially with an EPR spectrum obtained between evacuations. Following the third measurement, an addition of oxygen was made.

For the study of copper(II) aquo complexes in the Y zeolite, the copper ions were first reduced for 0.25 hr with 400 Torr H_2 at 673 K following the dehydration procedure. After reoxidation with 400 Torr O_2 for 0.25 hr at the same temperature and evacuation for 1 hr under a dynamic vacuum of 10^{-4} Torr, the sample was rehydrated by the addition of consecutive 20 Torr portions of water vapor to an equilibrium pressure of 2 Torr. The distilled, deionized water used had been previously purified of gaseous impurities by the freeze–thaw evacuation technique, and the additions were carried out at ambient temperature.

Physical Measurements

EPR spectra were recorded at 77 K in the X-band region by a Varian E-6S spectrometer equipped with a TE_{102} mode cavity. A sample of pitch in KCl was used as a reference standard for g-value determinations. Spin concentrations were calculated by numerical double integration of the spectra and comparison to a reference spectrum obtained with a single crystal of copper(II) sulfate. Although accuracies of ±30% are often stated for these calculations, through careful technique and the use of the standard pitch sample with each spectrum, better accuracy with good precision is obtainable, certainly within ±10%.

Calculations

For square coplanar and axially elongated octahedral Cu(II) complexes (D_{4h} symmetry), bonding parameters can be obtained from the EPR spectra of the complexes. The unpaired electron in this $3d^9$ case is assigned to the $3d_{x^2-y^2}$ orbital, and the overlap of this antibonding orbital with the ligand 2s and 2p σ orbitals is often determined by the use of equation 1 [20], where α^2 gives an approximate indication of the strength of the interaction between the metal and the ligands. P_o is the dipolar contribution to the hyperfine splitting value A, which is a negative quantity, and is usually assigned the free ion value of 0.036 cm^{-1} [21–23]. The constant term of K_o = 3/7 is equated to the Fermi hyperfine contact term of the free ion, which corrects for the Fermi contact contributions from excited state configurations of Cu(II), notably the $3s^1 3d^{10}$ and $3s^2 3d^8 4s^1$ configurations [23]. This is usually considered to be a constant term for Cu(II) square planar complexes since there is little ligand orbital density at the copper nucleus and the ratio of copper *s* to *d* character is assumed to be unchanged in the presence of ligands [20]. The addi-

$$\alpha^2 = |A_\parallel|/P_o + (g_\parallel - 2.0023) + K_o(g_\perp - 2.0023) + 0.04 \quad (1)$$

tion of 0.04 to the sum is an approximate correction due to the molecular orbital coefficients for the molecular orbitals of the complex that arise from in-plane π bonding (d_{xy}, β_1) and out-of-plane π bonding (d_{xz}, d_{yz}, β), where the π bonding is negligible and $\beta_1 = \beta = 1.0$ and where the in-plane σ bonding ($d_{x^2-y^2}$, σ) coefficient is about 0.9. Thus, α^2 represents the extent to which the unpaired electron resides on the central metal ion in the $d_{x^2-y^2}$ orbital (B_{1g} ground state) and reflects the extent of σ-bonding to the ligands. Consequently, a decline in the value of α^2 indicates an increase in the covalency of the bond.

In reality, P and K are not constant but vary as a function of the covalency of the bonds. These quantities can also be calculated from the experimental EPR parameters, where the following equations are used [24]:

$$A_{xx} = P[-2a_3 - K + 2/7 + 3/7(a_2)]$$
$$g_{xx} = 2 - 2a_3 \qquad (2)$$

$$A_{yy} = P[-2a_2 - K + 2/7 + 3/7(a_3)]$$
$$g_{yy} = 2 - 2a_2 \qquad (3)$$

$$A_{zz} = P[8na_1 - K - 4/7 - 3/7(a_2 + a_3)]$$
$$g_{zz} = 2 + 8na_1 \qquad (4)$$

In equations 4, n = +1 when the unpaired electron is assigned to the $d_{x^2-y^2}$ orbital, but equals −1 when the electron is assumed to be in the d_{xy} orbital, although this does not affect the resultant values. Using the experimental g values and the $A_{zz} = A_\parallel$ value, along with an empirical value of the Fermi contact term obtained from equation 5 [25] where $A_{iso} = 1/3(A_\parallel + 2A_\perp)$ and $g_{iso} = 1/3(g_\parallel + 2g_\perp)$, a corrected P value can be calculated by means of equation 4.

$$K = (A_{iso}/P) + (g_{iso} - 2.0023) \qquad (5)$$

Experimentally, $g_{xx} = g_{yy} = g_\perp$ for most of the complexes, and the hyperfine splittings A_{xx} and A_{yy} are not observed. However, an estimate of $A_\perp \approx 0.0018\ cm^{-1}$ can be made for the Cu(II) square planar complexes in Y zeolites. Using the corrected value of P, a new K value can be calculated using equation 5. This iterative procedure usually yields constant values for P and K in three cycles. The new values can then be used to calculate α'^2 by means of equation 1 where K_o and P_o have been replaced by the refined values. *CAUTION*: Trimethylphosphine is a highly toxic substance. If a slug of dioxygen is added rapidly to the copper(I) trimethylphosphine complex, a flash of fire occurs in the previously evacuated cell. This might represent an explosion hazard if the complex were present in large quantity.

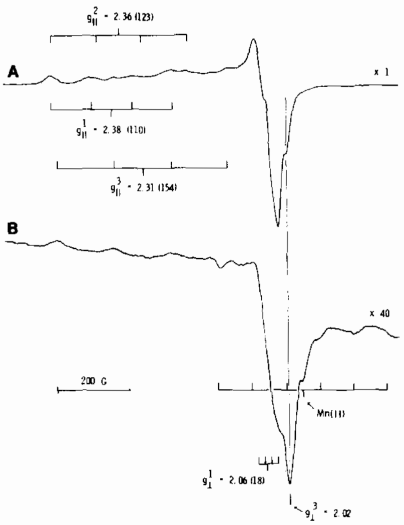


Fig. 1. The electron paramagnetic resonance spectra (obtained at 77 K) of CuY-10. (A) The zeolite was evacuated for 0.08 hr following stepwise activation to 773 K and oxidation with 250 Torr O_2 at that temperature for 0.5 hr. (B) At ambient temperature, 300 Torr trimethylphosphine was added and the sample was allowed to equilibrate for approximately 18 hr. The hyperfine splittings are given in parentheses in units of Gauss.

Results

The ion exchange procedure yielded a CuNaY zeolite in which 9.8% of the Na^+ ions were replaced by Cu(II) ion (designated as CuY-10). The light blue air-dried product contained 2.7 Cu(II) ions, about 50.6 Na^+ ions, and approximately 260 water molecules per unit cell, which yielded an approximate formula of $Cu_3Na_{50}(AlO_2)_{56}(SiO_2)_{136} \cdot 260H_2O$. Activation and oxidation at 773 K caused a color change to light green, and resultant solid produced the EPR spectrum A exhibited in Fig. 1. Oxidation was carried out to destroy any organic impurities and to reoxidize any copper ions that might have been thermally or chemically reduced. Addition of trimethylphosphine to the evacuated sample caused the CuY-10 to become white immediately. The EPR spectrum was greatly reduced in intensity with only one set of g values evident, a small sharp line a g = 2.00 appeared, and the 6-line spectrum of the Mn(II) impurity was evident (with hyperfine splitting of 93 G) under the higher magnification used to obtain the spectrum. Upon standing for 18 hr at ambient temperature, the sample exhibited spectrum B in Fig. 1, in which the g = 2.00 line had declined in intensity by 75–90%. Brief evacuations did not alter the spectrum.

Addition of excess oxygen to the sample at ambient temperature resulted in an instantaneous, highly exothermic reaction and the generation of an EPR spectrum with $g_\parallel = 2.44$ and $g_\perp = 2.05$ and

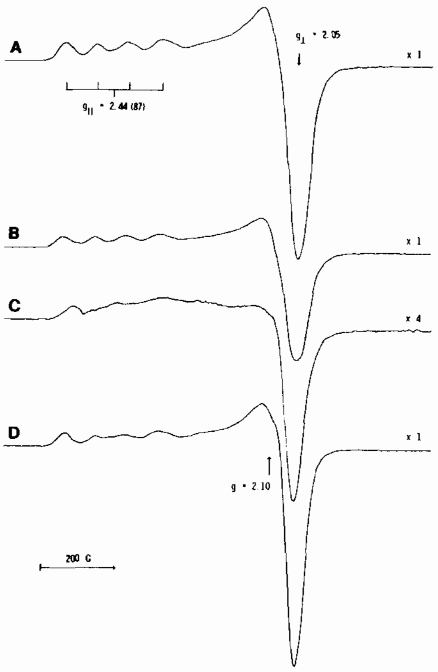


Fig. 2. The EPR spectrum (A) obtained 66 hr after adding 300 Torr O_2 to the sample tube (evacuated at 10^{-4} Torr for 0.05 hr) that contained CuY-10: trimethylphosphine. After the sample had equilibrated for an additional 264 hr, spectra B (77 K) and C (295 K) were obtained. Evacuation at ambient temperature for 0.02 hr produced spectrum D.

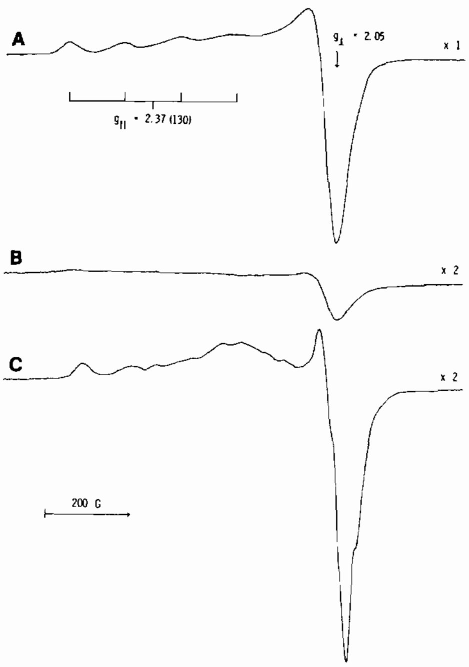


Fig. 3. CuY-10 was reduced with 400 Torr H_2 for 0.25 hr at 673 K after stepwise dehydration. After reoxidation with 400 Torr O_2 at 673 K for 0.25 hr, the sample was evacuated for 1 hr and then equilibrated for 1 hr under an equilibrium pressure of 2 Torr water vapor (A). Following reactivation to 673 K, the sample was equilibrated with 400 Torr O_2 at ambient temperature for 0.25 hr (B). Evacuating the sample (10^{-4} Torr and 295 K) for 1 hr yielded spectrum C.

with an intensity corresponding to complete recovery of the Cu(II) ions. A small sharp line at $g = 2.00$ was still evident, and considering the large reduction in spectral magnification, it appeared that this line must be due to a species generated during the reoxidation step. After allowing the sample to stand for 66 hr, the latter line disappeared from the EPR spectrum, as shown in Fig. 2. The species responsible for the $g = 2.00$ line is probably an organic radical generated by the thermal decomposition of a small amount of the trimethylphosphine ligand. Upon prolonged equilibration (11 days), the spectrum (Fig. 2B) was reduced in intensity and at ambient temperature the reduction in intensity was even more marked, as shown in Fig. 2C. In the latter case, the observed EPR parameters were shifted to the following values: $g_\parallel = 2.36$ and $A_\parallel = 125$ G. After a brief evacuation, the original EPR intensity (at 77 K) was recovered as evidenced by Fig. 2D. In addition, it appeared that a rhombic tensor was now present with $g_x = 2.10$.

For comparison, the EPR spectra of the CuY-10 system in the presence of a different oxygen ligand, *viz.* water, were obtained. Analogous to the previous reduction by the phosphine and reoxidation by O_2, a fresh zeolite sample was briefly reduced to the complete absence of Cu(II) ions with H_2 after activation and was subsequently reoxidized by O_2 at 673 K. Following rehydration, the EPR spectrum in Fig. 3A was obtained at 77 K. This spectrum was the same as that obtained for the sample prior to the initial activation. Equilibrating the hydrated sample under 400 Torr O_2 for 0.25 hr at ambient temperature and 0.25–0.5 hr at 77 K reduced the EPR spectral intensity by approximately 20%. Subsequent evacuation after warming to room temperature led to a partially dehydrated sample that yielded an EPR spectrum with two assignable $g_\parallel$ values and three assignable $g_\perp$ values. Similar spectra have been discussed elsewhere [15].

The copper(II) concentration determined from the integrated EPR intensity for the hydrated CuY-10 sample corresponded directly to the analytically determined copper content of the zeolite. However, the intensity of the spectrum obtained after reactivation and reoxidation (similar to Fig. 3C) yielded a Cu(II) content that was only about 70% that of the analytical concentration. The addition of 400 Torr O_2 to the sample further reduced the EPR intensity (spectrum B in

TABLE I. The Electron Paramagnetic Resonance Parameters of Copper(II) Phosphine Oxide Complexes.

Ligand	$g_\parallel$	$g_\perp = g_x$	g_y	$\lvert A_\parallel \rvert$ (10^{-4} cm^{-1})	$\lvert A_\perp \rvert$ (10^{-4} cm^{-1})	α^2	References
$(C_4H_9)_3PO$	2.414	2.079		87	16	0.73	29
$[(C_4H_9)_2PO]_2CH_2$^{a,b}	2.495	2.100		74.9		0.78	30
$[(C_4H_9)_2PO]_2(CH_2)_6$^{a,b}	2.422	2.103		118		0.83	30
$[((CH_3)_2N)_2PO]_2O$^{c}	2.52	2.08		90		0.84	31
$[((CH_3)_2N)_2PO]_2O$^{c}	2.52	2.12	2.06	90			31
$[((CH_3)_2N)_2PO]_2CH_2$^{c}	2.44	2.12					31
$[((CH_3)_2N)_2PO]_2O$^{b}	2.44	2.09					31
$[((CH_3)_2N)_2PO]_2CH_2$^{b}	2.50	2.08					31
$(CH_3)_3PO$	2.44	2.05		93		0.76	d
$(CH_3)_3PO$	2.44	2.10	2.05	93			d

^{a}Diluted in the corresponding zinc salt. ^{b}[ligand]/[Cu] = 2. ^{c}[ligand]/[Cu] = 3. ^{d}This Work.

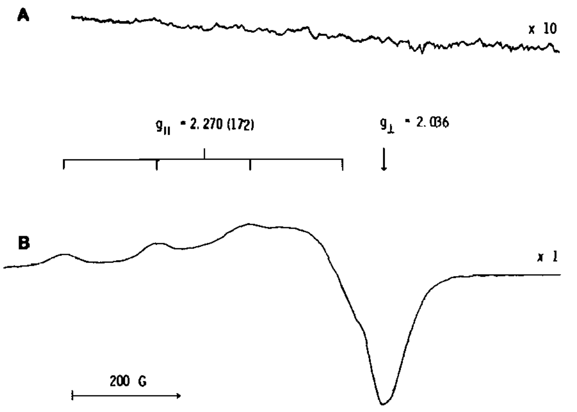


Fig. 4. The EPR spectra at 77 K obtained for CuY-10 following the described treatments: (A) following stepwise dehydration, reduction was carried out with 400 Torr CO and 25 Torr NH_3 at 673 K; and (B) addition of excess NH_3, evacuation for 0.5 hr after equilibrating for 1 hr, and allowing to stand at ambient temperature for 0.08 hr following the addition of 10 Torr O_2.

Fig. 3) by approximately 82% because of paramagnetic broadening of the spectrum. Spectrum 3C was obtained following evacuation of the sample for 1 hr at ambient temperature, for which the intensity was 98% of that of the reactivated CuY-10 and $g_\parallel^1 = 2.38$ (123), $g_\perp^2 = 2.06(18)$, $g_\parallel^3 = 2.32$ (157), and $g_\perp^3 = 2.02$.

A fresh portion of CuY-10 was activated by the step-wise procedure. Reduction was carried out for 3 hr at 673 K under a mixture of 25 Torr NH_3 and 400 Torr CO, where the purpose of the ammonia was to cause any Cu(II) ions in the small cages of the zeolite structure to easily migrate to the large cavities where they could readily be reduced by CO to Cu(I) [26]. The resultant solid was white and exhibited no Cu(II) EPR spectrum, as is shown in Fig. 4. Equilibrating with excess NH_3 for 1 hr caused no change. After evacuating at room temperature for 0.5 hr, 10 Torr O_2 was added. The sample became blue and spectrum B in Fig. 4 was obtained following equilibration for 0.08 hr at ambient temperature and 0.25 hr at 77 K. The addition of 200 Torr O_2 greatly broadened the spectrum. A spectrum very much like Figure 4B was obtained when 20 Torr NO was added as the oxidant rather than O_2, and a broadened spectrum that was reduced in intensity was produced in the presence of 120 Torr NO.

Discussion

After dehydration, ion exchanged Y zeolites containing divalent copper up to about 30% of its ion exchange capacity can exhibit three distinct sets of EPR parameters, and an example is presented in Fig. 1A. Previously, the g^1 set was assigned to copper(II) ions in exposed sites, such as locations in the supercage, and the g^3 set was attributed to Cu(II) ions in hidden sites in the small cages [15]. The g^2 set with a hyperfine splitting value generally in the 120–125 G range appeared to be due to Cu(II) ions in an intermediate location, perhaps site II′. Following the addition of trimethylphosphine to CuY-10, approximately 95% of the copper was reduced to the univalent state. Reduction to metallic copper would have yielded a pink sample [27], while this sample was white. Most of the unreduced copper was located in the small cages, as evidenced by the spectrum in Fig. 1B ($A_\parallel^3 = 155$ G), and it is obvious that the zeolite did not stabilize a copper(II)–trimethylphosphine complex in the trigonal windows. The initial activation, oxidation, and evacuation procedures employed were successful in achieving complete removal of molecular water and oxygen since the presence of these oxidants would have resulted in the immediate oxidation of the phosphine ligand.

The crystal structures of about 30 substituted phosphine–copper(I) compounds have been determined, and the only class without an example of known structure is L_4Cu^+ [28]. However, a tetrahedral geometry is expected, and the A, X, and Y zeolites should sufficiently stabilize the trimethylphosphinecopper(I) complex so that an X-ray structure determination could be carried out. Figure 2, in conjunction with Table I, demonstrates that in the presence of an oxidant both the cation and the ligand were oxidized. It is clear that the brief period of evacuation prior to the O_2 addition did not remove all of the trimethylphosphine. Even though excess oxygen was present, the EPR spectra in Fig. 2 were not significantly broadened at 77 K by paramagnetic interactions. Although spectrum 2C was greatly diminished in intensity, spin-lattice relaxation at the higher temperature did not broaden the spectrum to extinction.

The $g_{\parallel}$ value for the copper(II)–trimethylphosphine oxide complex is remarkably large while the $A_{\parallel}$ value is rather small. Table I demonstrates that this is generally observed for Cu(II) phosphine oxide complexes. The first study listed was carried out in solution, while the others were solid state preparations. The bonding parameter α^2 was calculated using eqn. 1. The EPR parameters are consistant for both the mono- and bidentate phosphine oxide ligand complexes with no regard to whether the coordination number of the copper was four or six with respect to the ligands of concern. The EPR data in Table I were obtained in the temperature range of 77–135 K, and it was observed that upon warming to ambient temperature, the g values for the bis$[((CH_3)_2N)_2PO]_2CH_2$ or -O copper(II) complexes did not change, although hyperfine splitting was then not observed [31]. Upon warming the tris$[((CH_3)_2N)_2PO]_2$-CH_2 or -O complexes to 297 K, the EPR spectra collapsed into symmetric lines, and that behavior was attributed to a dynamic Jahn–Teller effect [31]. As indicated in Fig. 2C, similar behavior was not observed in the trimethylphosphine oxide copper(II) Y zeolite system, where a diminution in intensity occurred at 297 K but the generation of a symmetric line was not evident.

TABLE II. The Electron Paramagnetic Resonance and Derived Bonding Parameters of Divalent Copper($3d^9$) Complexes in Y Zeolites.

Complex	$g_{\parallel}$ [a]	$g_{\perp}$	α_i^2 [b]	$\lvert A_o \rvert$ [c]
$Cu(C_5H_5N)_4^{2+}$	2.24 (198)	2.03	0.84	78
$Cu(NH_3)_4^{2+}$	2.27 (184)	2.04	0.84	74
$Cu(H_2O)_4^{2+}$	2.32 (171)	2.03	0.85	70
$Cu[OP(CH_3)_3]_4^{2+}$	2.44 (93)	2.05	0.76	43

[a] The numbers in parentheses are the hyperfine splitting values in units of cm^{-1} ($\times 10^4$). [b] Calculated on the basis of square planar geometry. [c] $\times 10^4$ cm^{-1}; assumed that $A_{\perp} \approx 0.0018$ cm^{-1}.

The spectrum in Fig. 3A is due to $Cu(H_2O)_6^{2+}$ [15], while the spectrum in Fig. 4B is attributed to square planar $Cu(NH_3)_4^{2+}$ [32]; both complexes are located in the supercages of the Y zeolite structure. Sample treatments of the zeolites in this investigation consisted of evacuatiom, activation, and reduction utilizing various reducing agents. In the CO reduction, NH_3 was employed as a complexing agent to draw the divalent copper ions out of the small zeolite cages into the supercages where reduction occurred. Following reduction, it appeared that $Cu(NH_3)_n^+$ complexes, where n is probably 1 or 2, were stabilized in the supercages since immediate reoxidation took place upon the addition of oxygen. For samples prepared such that the Cu^+ ions were deliberately placed in the small cages, *e.g.* by prolonged evacuation and subsequent activation and reduction in the absence of NH_3, reoxidation was slow [33]. Upon addition of 200 Torr O_2 to the present zeolite, the EPR spectrum due to $Cu(NH_3)_4^{2+}$ was greatly broadened. This was to be expected since paramagnetic oxygen molecules can approach the square planar ammine complex from the axial directions. In contrast, the $Cu(H_2O)_6^{2+}$ spectrum suffered much less broadening, but the 'uncomplexed' Cu(II) ions in the activated Y zeolite exhibited a loss of about 90% of their EPR intensity upon O_2 addition (Fig. 3B). The trimethylphosphine oxide complex showed the least broadening. This indicated that the complex was held in the zeolite supercages in a configuration that hindered the close approach of oxygen molecules.

This configuration would be expected to affect the bonding parameters of the complex, and the α^2 values for a number of tetrakis Cu(II) complexes in Y zeolites are given in Table II. It is assumed that the trimethylphosphine oxide complex is 4-coordinate because the hexacoordinate complex would be too large to fit into the supercages. The EPR parameters of the $Cu(H_2O)_4^{2+}$ [15] and $Cu(C_5H_5N)_4^{2+}$ [34, 35] complexes were reported elsewhere. The hyperfine splitting for the ammine complex falls in the range of values usually observed, 180–187 $\times$ 10^4 cm^{-1} [32]. A consideration of the initial α^2 values indicated that the oxygen ligands form stronger covalent bonds (lower α^2 values) than do the nitrogen ligands. However, in the terminology of the hard and soft acid and base theory [36], Cu(II) and the various N ligands are intermediate in strength, while O ligands are hard bases. Therefore, N donors are considerably

TABLE III. The Parameters Calculated from the EPR Spectra of the Tetrakis Complexes.

Complex	α_i^2	K_{est}	K^a	P^b	α'^2
$Cu[OP(CH_3)_3]_4^{2+}$	0.76	0.33	0.42	0.018	1.02
$Cu(H_2O)_4^{2+}$	0.85	0.37	0.37	0.029	0.96
$Cu(NH_3)_4^{2+}$	0.84	0.36	0.36	0.029	0.95
$Cu(C_5H_5N)_4^{2+}$	0.84	0.36	0.34	0.029	0.89

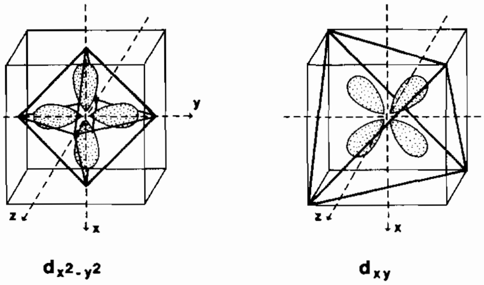
[a] $K_o = 0.43$. [b] $P_o = 0.036\ cm^{-1}$.

softer than are O donors, and stronger covalent bonding would be expected with the N ligands; this is generally observed, *e.g.* $-\Delta G_f^\circ$ values for Cu(II)–N complexes are approximately double the values found for the formation of analogous Cu(II)–O complexes, with both uni- and bidentate ligands [36]. The effect of increased electron-donating ability, *e.g.* with a series of β-diketonate complexes of divalent copper [37], on the EPR parameters is to decrease $g_\parallel$ and increase $A_\parallel$. As a point of interest, Cu(I) is a soft acid and P is a softer base than is N, and therefore a rather strong stable covalent trimethylphosphine copper(I) complex would be expected in the zeolite.

From another point of view and in consideration of equation 1, α^2 should decrease as $A_\parallel$ decreases and should also decrease with decreasing $g_\parallel$ and $g_\perp$. Thus, enhanced covalent bonding would be expected as g_{iso} approaches 2.0023. This is not the trend that is evident in Table II, where the g value trend is contrary to the calculated covalency trend. In seeking an explanation, it is noted that tempering factors include both P and K values. As covalency increases, the Fermi contact coupling (K) of the electron and copper spins should no longer be equivalent to the free ion value (K_o) where $\alpha^2 = 1$. Rather, K would be expected to be somewhat smaller in magnitude and can be estimated by utilizing eqn. 6. The electron–nuclear dipolar coupling contribution (P) would also be expected to be less than the free ion value.

$$K_{est} = \alpha_i^2 \cdot K_o \tag{6}$$

The 'refined' values are tabulated in Table III, where α_i^2 is the initial covalency value calculated by eqn. 1. Clearly, the calculation process is not valid for the $Cu[OP(CH_3)_3]_4^{2+}$ complex since a 0% covalency is not expected in light of the greater stability of the complex toward decomposition by evacuation in comparison to the other three complexes listed. In contrast, the latter three complexes yield reasonable refined K and P values, and the α'^2 values are now in the order expected in regard to the experimental g values.



$d_{x^2-y^2}$ d_{xy}

Fig. 5. Illustrations of the $d_{x^2-y^2}$ and d_{xy} orbitals that would contain the unpaired electron on copper(II) when in the square coplanar and pseudotetrahedral configurations, respectively.

Since the dipolar coupling contribution P is characteristic of the types of ligands and of the covalency of the complex, P would indicate a rather covalent complex if the trimethylphosphine oxide complex were square coplanar. The small hyperfine splitting value indicates a high delocalization of the unpaired electron on the copper ion, and this could be achieved by a significant amount of 4p orbital mixing into the ground state. This mixing could occur if the copper(II) complex were distorted toward a tetrahedral configuration. In addition, the admixture of 4s character into the ground state in noncentrosymmetric complexes provides a positive contribution to the negative nuclear hyperfine splitting [38] and reduces the absolute magnitude of the observed hyperfine splitting values. The pseudotetrahedral configuration would also yield large $g_\parallel$ values since coupling between the $d_{x^2-y^2}$ and d_{xy} orbitals could occur. Indeed, if the distortion were large enough, the unpaired electron would be localized in the d_{xy} orbital (shown in Fig. 5) since the lobes of this orbital would then be approached by the ligands. It has been reported that in pseudotetrahedral copper(II) complexes very small compression changes can alter the 'ground state' d orbital from one d orbital to another [39].

From physical considerations, it might be expected that the copper(II) trimethylphosphine oxide complex in Y zeolite would be distorted toward a tetrahedral configuration. The diameter of the supercage cavities in the zeolite lattice are on the order of 1.3 nm. If the complex were square coplanar with linear Cu–O–P angles, the diagonal dimension of the complex would be somewhat greater than the available space. Bent Cu–O–P angles would decrease the diameter of the complex, but steric crowding would still occur. A configuration intermediate between those shown in Fig. 5 would improve the fit with or without bent Cu–O–P moieties. It is of interest to note that the dichloro- and dibromobis(triphenylphosphine oxide)copper(II) compounds [40, 41] have both distorted tetrahedral symmetry around the copper ion and bent Cu–O–P angles.

This investigation has demonstrated that copper ions held in Y zerolites have rather high mobilities, readily undergo reduction by trimethylphosphine to form stable copper(I) complexes, which are subsequently easily oxidized to copper(II) trimethylphosphine oxide ions held in the supercages of the Y zeolite. The Cu(II) ions having EPR parameters of $g_{\parallel}^{3}$ = 2.31 (154) and $g_{\perp}^{3}$ = 2.02 have been established to be localized in the sodalite cages where some of the ions resist reduction by the trimethylphosphine ligand. The trimethylphosphine oxide copper(II) complex is appreciable more resistant to paramagnetic broadening by oxygen than are the tetrammine, hexaquo, and lattice-held Cu(II) ions. This is probably due to the large size of the oxide complex, which more-or-less fills the supercage, and to its pseudotetrahedral configuration.

For a Cu(II)N_4 coordination system, it had been previously reported that $A_{\parallel}$ decreased and $g_{\parallel}$ increased as the total positive charge on these five atoms increase [42]. Elsewhere, it was demonstrated that at constant charge, the same type of relationship arose via tetrahedral distortion [43]. This is reminiscent of the behavior observed with the 'blue' (type I) copper proteins [44]. Although the α'^2 values in Table III appear to be in the expected order, they appear to be too high. This might be due to a finite deviation from square coplanar symmetry for the 4-coordinate complexes, and this deviation could account for the antiparallel behavior between the g values and the α^2 values (which can be strictly calculated only for square coplanar complexes) that is evident in Table II for the nitrogen and the oxide complexes since the antiparallelism would be markedly enhanced by increased distortion toward tetrahedral symmetry. Thus, from this discussion and the examples presented, for 4-coordinate copper(II) complexes two series of covalency in terms of the EPR parameters can be set up. For square coplanar complexes, $g_{\parallel}$ decreases and $A_{\parallel}$ increases as the covalency increases (and α^2 decreases), where the O-donor complexes have higher g values but smaller A values than the analogous N-donor complexes, while $g_{\parallel}$ increases and $A_{\parallel}$ decreases as the covalency of pseudotetrahedral copper(II) complexes increases, and the same arguments could be applied to g_{iso} and A_{iso}. The tetrakis(trimethylphosphine oxide) copper(II) complex belongs to the second series consisting of complexes with pseudotetrahedral symmetry.

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