Title	ESR Study of the pH Effect on Cupric Complexes in Saturated Ammonium Sulfate Aqueous Solution
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Citation	北海道大學工學部研究報告, 105, 109-116
Issue Date	1981-07-31
Doc URL	https://hdl.handle.net/2115/41689
Type	departmental bulletin paper
File Information	105_109-116.pdf

北海道大学工学部研究報告
第105号（昭和56年）

Bulletin of the Faculty of Engineering,
Hokkaido University, No. 105 (1981)

ESR Study of the pH Effect on Cupric Complexes in Saturated Ammonium Sulfate Aqueous Solution

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(Received March 31, 1981)

Abstract

The effect of pH on Cu^{2+} ion site selection in ammonium sulfate single crystals grown from mother solutions was clarified. It was confirmed that Cu^{2+} ions on substitutional sites in a crystal grown from an acidic solution originate from a $[Cu\ (H_2O)_6]^{2+}$ complex in the solution and at the same time ions on interstitial sites in a crystal grown from either a neutral or an alkaline solution originate from a $[Cu\ (NH_3)_n\ (H_2O)_{6-n}]$ complex in the solutions. Spin-Hamiltonian parameters were determined for $[Cu\ (H_2O)_6]^{2+}$ and $[Cu\ (NH_3)_4\ (H_2O)_2]^{2+}$ complexes. The ratio of radius R, derived from the observed correlation times for the former complex and the latter was found to be 1. 7. Two trapping mechanisms to explain the site selection were proposed.

Introduction

There are disagreements among the reported ESR parameters, determined for the Cu^{2+} doped ferroelectric material, $(NH_4)_2SO_4$. From ESR measurements on Cu^{2+} doped $(NH_4)_2SO_4$ performed by Matsuki, Ohno and Sohma[1,2] the effect of pH of mother solutions on Cu^{2+} ion site selection has been found and this pH effect may be one of the reasons for the discrepancy found among the literatures, in which much attention has not be paid to the pH of the mother solutions. The results indicate that Cu^{2+} ions are trapped in substitutional sites in single crystals grown from acidic solution and, on the other hand, those are trapped in interstitial sites between two adjacent NH_3 ions in crystals grown from neutral solution. Moreover a Cu^{2+} ion substitutionally located on an ammonium ion site needs a vacant NH_4^+ site for charge compensation, while for Cu^{2+} ion occupying an interstitial site charge excess is compensated in such a way that each of its two neighboring ammonium ions lacks one proton. Such difference in charge compensation mechanism is consistent with the difference in pH of the mother solution. It was presumed as follows. Cu^{2+} ions are coordinated with ammonium ion in either alkaline or neutral solution, where two ammonium ions are easily replaced by

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a single Cu^{2+} ammonium complex and the Cu^{2+} ion is consequently located on an interstitial site in this replacement. Cu^{2+} ions are not coordinated with ammonium ions in the acidic solution[3] where the ammonium ion in the crystal is easily replaced by a Cu^{2+} ion.

The present investigation was designed to determine the ESR parameters of Cu^{2+} ions in solutions of different pH regions and to ascertain the effect of pH on the Cu^{2+} site selection.

Complexes of Cu^{2+} are quite amenable for a study by ESR and seem probably the most studied transition metal ion. Apart from a few salts with trigonal symmetry, the majority of the hydrated salts of copper contain a $[Cu(H_2O)_6]^{2+}$ complex with a distortion of tetragonal or somewhat lower symmetry in which typical g-values are $g_\perp \sim 2.4$, $g_{//} \sim 2.1$.[4] These values shows that in a tetragonal approximation, the singly occupied orbital should be $d_{x^2-y^2}$. From X-ray analysis for copper perchlorate aqueous solution, the distance from the central ion to H_2O in a square planar plane was determined *to be 1.94 Å and that to the upper (or lower)* H_2O *to be 2.43 Å.* The additional tetragonal distortion to octahedron is due to the John-Teller effect.

Experimental

Commercial extra pure ammonium sulfate (Wako Junyaku Co. Ltd) and copper tetrafluoroborate (Alfa Division) were used to prepare copper complexes in saturated $(NH_4)_2SO_4$ aqueous solutions. The pH of the solution was controlled by adding NH_4OH aqueous solution. The ESR spectra of the copper complexes were measured in 10^{-3}M solution both at room and liquid nitrogen temperatures with a JEOL-PE-1X X-band, ESR spectrometer with a 100Hz field modulation.

Results and Discussion

The ESR spectra drastically changed from acidic to neutral solutions at room temperature, whereas no such changes were found between neutral and alkaline solutions, as shown in Fig. 1. In acidic solutions, the spectra have four hyperfine lines with such spin-dependent broad linewidths that they overlap with each other to produce complicated spectra. In addition, a small amount of other unidentified cupric complexes exists in the solutions and the mixing makes their spectra slightly more complicated, *especially in the acidic region. In acidic solution as* m_I increases, the nuclear spin-dependent linewidths are reduced to about a half value at $m_I = -3/2$ which is comparable with the hyperfine coupling constant. On the other

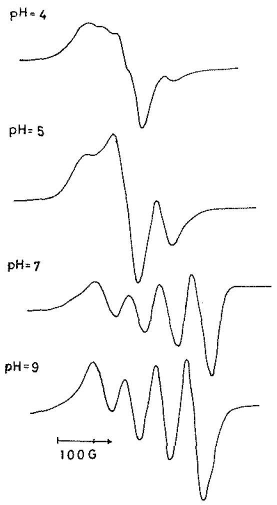


Fig. 1 Liquid phase spectra of the cupric complexes at various values of pH.

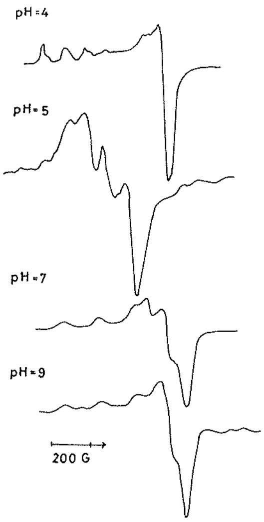


Fig. 2 Solid phase ESR spectra of the cupric complexes at various values of pH.

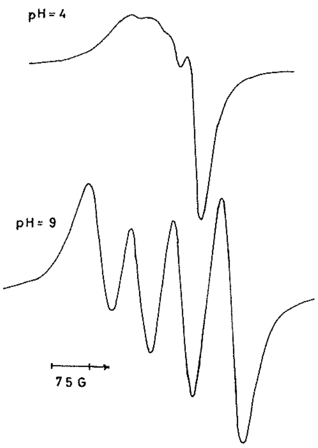


Fig. 3 Simulated spectra for liquid phase solutions at pH=4 and 9.

hand, the decreasing rate of linewidth in the alkaline solution are considerably small.

Eig. 2 displays amorphous ESR spectra of the cupric complexes at 77K. The spectra in both liquid and solid phases demonstrate the existence of more than two complexes in the pH regions from 5 to 7 and an analysis of the complicated spectra are actually difficult or impossible. At 77K, the spectra consist of characteristic patterns with intensive anisotropic g and hyperfine couplings and give twice as large hyperfine coupling at pH=9 than at pH=4. Considering such a complication, the two spectra at pH=5 and 9 were treated with hereafter. The isotropic g_0 and a were obtained from the liquid spectra using simulation methods. The $g_{/\!/}$ and $A_{/\!/}$ were directly determined from the spectra.[5] The values of $g_{/\!/}$ and $A_{/\!/}$ were evaluated using both the following relations and the observed values for $g_{/\!/}$, g_0, $A_{/\!/}$ and a.

$$g_0 = \frac{g_{/\!/} + 2g_{\perp}}{3} \qquad (1)$$

Table I. ESR parameters for the cupric complexes in acidic and alkaline saturated ammonium sulfate solutions.

Complex	g_0	$g_{/\!/}$	$g_{\perp}$	a (cm^{-1})	$A_{/\!/}$ (cm^{-1})	$A_{\perp}$ (cm^{-1})
$[Cu(H_2O)_6]^{2+}$	2.168	2.353	2.076	-3.54×10^{-3}	-1.16×10^{-2}	0
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	2.120	2.256	2.051	-7.76×10^{-3}	-1.95×10^{-2}	2.38×10^{-3}

$$a = \frac{A_{/\!/} + 2A_{\perp}}{3} \tag{2}$$

Here the signs of $A_{/\!/}$ and $A_{\perp}$ were taken to be negative. These values are listed in Table I. Based on the $g_{/\!/}$ and $g_{\perp}$ values it is concluded that in an octahedral field with tetragonal distortion, the orbital ground state must be $|\,2s\rangle$ (i. e. $d_{X^2-Y^2}$ state).[5,7,8] By group theory the proper linear combination of ligand orbitals can be combined with the copper d orbitals to form the following antibonding wavefunctions, $\psi_{B_{1g}}$, $\psi_{B_{2g}}$, $\psi_{A_{1g}}$, and ψ_{Eg}.

$$\psi_{B_{1g}} = \alpha d_{X^2-Y^2} - \frac{1}{2}\alpha'[-\sigma_X^{(1)} + \sigma_y^{(2)} + \sigma_X^{(3)} - \sigma_y^{(4)}] \tag{3}$$

$$\psi_{B_{2g}} = \beta d_{xy} - \frac{1}{2}(1-\beta^2)^{1/2}[P_y^{(1)} + P_X^{(2)} - P_y^{(3)} - P_X^{(4)}] \tag{4}$$

$$\psi_{A_{1g}} = \gamma d_{3z^2-r^2} - \frac{1}{2}(1-\gamma^2)^{1/2}[\sigma_X^{(1)} + \sigma_y^{(2)} - \sigma_X^{(3)} - \sigma_y^{(4)}] \tag{5}$$

$$\delta d_{xz} - (1-\delta^2)^{1/2}[P_z^{(1)} - P_z^{(3)}] / \sqrt{2} \tag{6}$$

$$\psi_{Eg} =$$

$$\delta d_{yz} - (1-\delta^2)^{1/2}[P_z^{(2)} - P_z^{(4)}] / \sqrt{2} \tag{7}$$

Overlap is included only for the $\psi_{B_{1g}}$ state, where α and α' are related.

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha' S = 1 \tag{8}$$

Here S is the overlap integral. In all other cases the overlap integrals were assumed to be small and were neglected. In these wavefunction the σ orbitals are hybridized hence orbitals of the type

$$\sigma = np \mp (1-n^2)^{1/2} s \tag{9}$$

where the minus sign refers to those ligands along the position x and y axis and $0 \leq n \leq 1$. Our interest is determing these bonding parameters which are related to observable ESR parameters. When the wave function for the B_{1g} state is applied to the Hamiltonian assuming an axial field and taking into account only the Zeeman term with an anisotropy in g, and the hyperfine terms with their anisotropies,

$$H = g_{/\!/}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{/\!/} S_z I_z + A_{\perp}(S_x I_x + S_y I_y) \tag{10}$$

the ESR parameters obtained are given in the following relations.

$$g_{/\!/} = 2.0023 - (8\lambda/\Delta E_{xy})\ [\alpha^2\beta^2 - f(\beta)] \tag{11}$$

$$g_{\perp} = 2.0023 - (2\lambda/\Delta E_{xz})\ [\alpha^2\delta^2 - g(\delta)] \tag{12}$$

$$\begin{aligned} A_{/\!/} &= P[-\alpha^2(\frac{4}{7} + K) - 2\,\lambda\alpha^2(\frac{4\beta^2}{\Delta E_{xy}} + \frac{3}{\eta} \cdot \frac{\delta^2}{\Delta E_{xz}})] \\ A_{\perp} &= P[\alpha^2(\frac{2}{7} - K) - \frac{22}{14} \cdot \frac{\lambda}{\Delta}\ \frac{\alpha^2\delta^2}{\Delta E_{zz}} \end{aligned} \tag{13}$$

where

$$f(\beta) = \alpha\alpha'\beta^2 S - \alpha\alpha'\beta(1-\beta^2)^{1/2}\tau(n)/2 \tag{14}$$

Table II. Bonding parameters for the cupric complexes.

Complex	α	α'	β	δ
$[Cu(H_2O)_6]^{2+}$	0.84	0.24	0.95	1
$[Cu^{2+}(NH_3)_4(H_2O)_2]^{2+}$	0.88	0.41	0.95	0.8

$$g(\delta)\ =\alpha\alpha'\delta^2S+\alpha\alpha'\delta(1-\delta^2)^{1/2}\tau(n)/\sqrt{2}, \tag{15}$$

λ is the spin-orbit coupling constant for the free ion, $P=2\gamma_{Cu}\beta_O\beta_N < d_{x^2-y^2}|\frac{1}{r^3}|d_{x^2-y^2}> =0.036\ cm^{-1}$, $\gamma_{C}u$ is the magnetic moment of copper nuclei (Cu^{63} or Cu^{65}), β_O is the Bohr magneton, and β_N is the nuclear magneton. The constant k, introduced by Abragam and Pryce, corrects for the Fermi contact term of excited configurations of copper, notably the $3s3d^{10}$ and $3d^84s$ configurations. The constant $\tau(n)$ is an integral over ligand functions and arises from the calculation of the matrix elements of the Hamiltonian with the wave functions.

If the ligand contains nuclei with non zero spin, an extra-hyperfine must be included for the hyperfine interaction though a dipole-dipole term between the electron and the nuclear magnetic moments must be taken but can be assumed to be small. The Fermi term depends on the amount of electron spin reaching the ligand and hence on α'. The isotropic Fermi term gives the interaction energy:

$$W_L=\frac{4\pi}{9}\gamma_L\beta_0\beta_N\alpha'^2|\rho(0)|^2S_zI_{zL} \tag{16}$$

where γ_L is the magnetic moment of the ligand atom and $|\rho(0)|^2$ is the value of ligand 2s function at the ligand nucleus. Maki and Mc Garvey[7] have estimated $|\rho(0)|^2$ for nitrogen to be $33.4\times10^{24}\ cm^{-3}$. Kivelson and Neiman[8] have given an approximate formula for α based on $A_{/\!/}$.

$$\alpha^2=-(A_{/\!/}/P)+(g_{/\!/}-2)+\frac{3}{7}(g_{\perp}-2)+0.04 \tag{17}$$

Here it must be noted that (4/7)+K=1.0, Equation (17) can be used to obtain a first approximation of α^2. The parameter α' was then calculated from Eq. (8). From $g_{/\!/}$, α, α' and the ligand field energies we calculated β. The parameter δ was calculated from Eq. (12) using the above obtained values.

Electron spin resonance spectra show a very wide range of linewidth effects, from which the most useful physico-chemical information can be obtained. Very generally, we can distinguish two main sources of line broadening; one involves essentially chemical interaction of the radicals, and the other does not. The latter are more fundamental in that the spectrum of anything in solution has lines of finite width, determined by the modulation of the various magnetic interactions as the molecules tumble about, and we can assume a certain basic linewidth, or natural linewidth from this source. Quantitative analysis of this linewidth may reveal information about the magnetic interactions within the species and the manner of the motion of the species in the solution. If the species is undergoing some kind of chemical process in addition, there may be a contribution to the linewidths from this source and the analysis of this may yield information about its rate and mechanism. In the present work, however, the contribution of chemical exchange can be neglected because in both limits of pH range the concentrations of other complexes were small enough in comparison with those of complexes under investigation when the complex is moving rapidly in a solution of low viscosity, the spectral anisotropies almost are averaged out to increase linewidths and, the line shape of which is Lorentzian. Under this condition, the linewidth can often be fitted to an expression of the form

$$1/T_2 = A + Bm_I + Cm_I^2 \qquad (18)$$

or $$1/T_2 = \tau_R \left\{ [3I(I+1)+5m_I^2]\frac{b^2}{40} + \frac{4}{54}(\Delta\gamma H)^2 - \frac{4}{15} b \Delta\gamma H m_I \right\} \qquad (19)$$

where

$$b = \frac{4}{3}\pi(A_{/\!/} - A_{\perp}), \qquad \Delta\gamma = -|\beta|\, h^{-1}(g_{/\!/} - g_{\perp}). \qquad (20)$$

The correlation time τ_R may be derived from the viscosity, η, assuming a spherically symmetrical solute molecule (radius, R) and Stokes law viscosity

$$\tau_R = 4\pi\eta R^3/3kT \qquad (21)$$

Other contributions from the spin-rotational interaction, the perturbation of solvation, the nuclear quadrupole interaction and the translational interaction of ligands should be taken into account in the first term. The determined parameters of Eq. (18) with the use of the least mean square method are listed in Table III. Substituting Eq. (2) into Eq. (19) and making it equal to Eq. (18).

$$\tau_R = \frac{9c}{2\pi^2 (A_{/\!/} - A_{\perp})^2} \qquad (22)$$

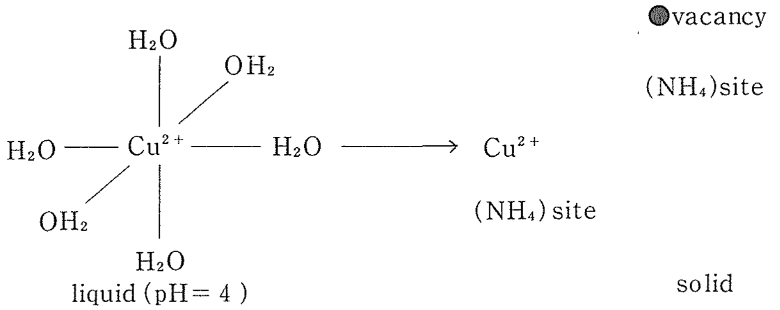
Using $A_{/\!/}$ and $A_{\perp}$ obtained from the present work, $(\tau_R)_{\text{acid}}$, $(\tau_R)_{\text{alkaline}}$ and the ratio of τ_R for acidic solution to that for alkaline one was calculated to be 6.6. The viscosities of 1.72 and 1.70 poise for each solution were measured at 20℃ and were taken as in the same magnitude within experimental errors. From values of C, $A_{/\!/} - A_{\perp}$, and η or the determined τ_R's, the hydrodynamic radii were calculated to be 2.20Å

Table III. Spin-dependent linewidths ($\times 10^3$ cm^{-1}) at 12°C.

Complex	m_I				coefficients		
	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	A	B	C
$[Cu(H_2O)_6]^{2+}$	6.58	5.26	4.25	3.24	4.74	−1.10	7.59×10^{-2}
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	4.95	4.62	4.16	3.96	4.38	-3.43×10^{-1}	3.27×10^{-2}

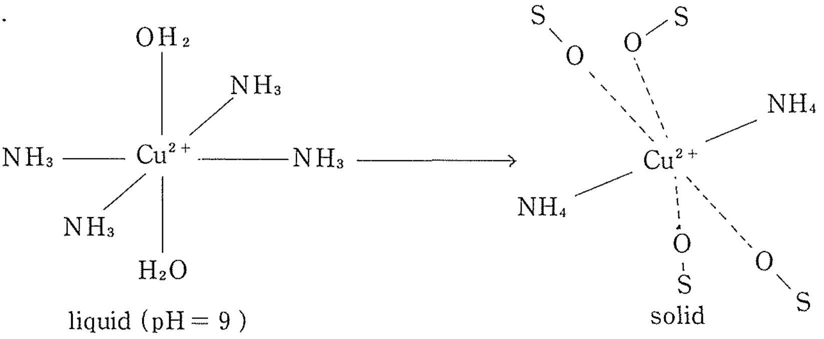
and 1.12Å for $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ respectively. That is, the radius for the former is 1.9 times larger than that of the latter. This indicates that the coordinated water molecule gives rise to a larger radius than the ammonia molecule does because the radius R involves effects from the second ligand layer and the contribution from the second layer is predominant in the case of $[Cu(H_2O)_6]$ than $[Cu(NH_3)_4(H_2O)]$.

In terms of electrostatic, neutral molecules (H_2O, NH_3, etc.) are bound to metal ions through the attraction between the negative end of the ligand dipole and the metal cation. The more polar the ligand, the greater should be the force binding the ligand and metal ion. Water is the most polar of the common ligands and hence would be expected to form metal complexes of greater stability than other neutral ligands. However, the greater the base strength of a ligand, the greater is the tendency of the ligand to form stable metal complexes. Ligand that bind H^+ firmly should also form stable complexes with metal ions. From this point of view NH_3 should be a better ligand than H_2O. The electrostatic contributions are still important but other factors, crystal field effects and covalent bonding are also important. Cu^{2+} prefer NH_3 to H_2O as a ligand because NH_3 provides a greater crystal field than H_2O. This explanation is probably given into crystalization grown from mother solutions involving different stable metal complexes. A mechanism (I) is proposed for the acidic mother solution, in which



(I)

metal cation can release ligand water molecule easier than ligand ammonia molecule and are trapped on (NH_4) site accompanying vacancy to compensate charge neutralization.



(II)

A different mechanism (II) is proposed for neutral and alkaline mother solutions, in which the ammonia molecule is bound to the metal cation more firmly than water molecule is trapped on the crystal surface together with Cu^{2+} ion.

Conclusion

When ammonia is added to saturated $(NH_4)_2SO_4$, more water coordinated to the metal ion are replaced by ammonia, as the concentration of ammonia increases. By ESR measurement, $[Cu(H_2O)_6]$ and $[Cu(NH_3)_4(H_2O)_2]$ complexes were confirmed and spin Hamiltonian parameters and linewidths regarding these two complexes were also determined. Anisotropic *g* and hyperfine coupling constants indicate that both two complexes have an octahedral field with tetragonal distortion. The bonding parameters for ligand molecules were also determined. The analysis of linewidth resulted in the ratio of radius R of 1.7 which suggests the effective radius for $[Cu(H_2O)_6]^{2+}$ complex is larger than that for $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex. It was ascertained that the pH effect of cupric ion on site selection in single crystals depends upon the difference of stability of ligand molecules.

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