Electron Spin Resonance Studies of Bis(acetylacetonato)copper(II) Adsorbed on X-Type Zeolite. II. The Substitution Reaction of Ligands with Pyridine

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The interaction of bis(acetylacetonato)copper(II) (Cu(acac)$_2$) adsorbed on X-type zeolite of the sodium form with pyridine was investigated by means of ESR. When a pyridine vapor was introduced to Cu(acac)$_2$ on the zeolite, the spectral lines of the perpendicular g component for Cu(acac)$_2$ were replaced by those consisting of a superhyperfine structure, which arises from the ligand nitrogen atoms. The observed spectrum was assigned to [Cu(pyridine)$_4$]$^{2+}$. Such a characteristic substitution reaction of Cu(acac)$_2$ with pyridine was not, however, observed on silica gel nor in ordinary solvents. It is pointed out, on the basis of these results and of the considerations described in a preceding paper, that the reaction involves the following mechanism: the interaction of quasi-π-electrons in Cu(acac)$_2$ with an electrostatic field originating from the cation on the zeolite lowers the stability of Cu(acac)$_2$, and the complex is attacked by two adsorbed pyridine molecules and two pyridinium ions which are formed by the combination with protons on acid sites, resulting in the substitution reaction. In addition, [Cu(pyridine)$_4$]$^{2+}$ was produced on other cation-exchanged zeolites and silica-alumina. The substitution reaction was also found when α-, β-, or γ-picoline was used instead of pyridine.

The interaction of adsorbed bis(acetylacetonato)copper(II) (Cu(acac)$_2$) with the surface and the effect of ammonia and aniline on the complex were studied in the preceding paper (hereafter to be designated as part I). With regard to the interaction with pyridine, we[1] have recently reported that a ligand-substitution reaction occurs on the introduction of pyridine to Cu(acac)$_2$ adsorbed on the zeolite. Yokoi *et al.*[2] have found a substitution reaction with pyridine in the solution of bis(ethylacetoacetato)copper(II) or bis(salicylaldehydrato)copper(II). They have pointed out, however, that Cu(acac)$_2$ brings about no substitution reaction with pyridine in a chloroform solution. It is known, with respect to Cu(acac)$_2$ and other copper(II) β-diketone chelate complexes, that some heterocyclic bases coordinate to the complex as one or two apical ligands in ordinary solvents, such as chloroform or toluene, and that an adduct is formed.[2-6] Therefore, in order to explain the difference between the reactivity of the complex on the surface and that in solution, a reaction mechanism is proposed on the basis of the influence of the surface, and, at the same time, the assignment attempted in the short communication[1] is reconsidered in the present work.

Experimental

The X-type zeolite of the sodium form (NaX zeolite) is the same as that used in part I. The cation-exchanged zeolites, NH$_4$X (NH$_4$X may not be a precise representation, because ammonia gas is released from NH$_4$X zeolite by the evacuation at 500°C and protons are considered to be present on the surface.), LiX, and CaX, were prepared from the original NaX zeolite by the conventional method.[7] The amount of the sodium ion exchanged was determined by means of atomic-absorption spectroscopy. The percentage of the exchanged cation was 96.1, 86.0, or 94.4 for NH$_4$X, LiX, or CaX respectively. Silica-alumina (alumina content *ca.* 40%) was synthesized from ethyl orthosilicate and aluminum isopropoxide. GR-grade pyridine was further purified by distillation under a vacuum. The IR spectra were obtained using a Hitachi EPI-S2 spectrophotometer. The preparation of the other samples and the procedure of the measurements have been described in part I.

Results and Discussion

The Formation of [Cu(pyridine)$_4$]$^{2+}$ on NaX Zeolite. When Cu(acac)$_2$ adsorbed on NaX zeolite was exposed to pyridine vapor at room temperature, the spectrum presented in Fig. 1 (a) was observed. This spectrum differs remarkably at the perpendicular g component ($g_\perp$) from that due to Cu(acac)$_2$ on the zeolite, which has been shown in Fig. 1 (a) of part I. The variation in the spectrum suggests the conversion of Cu(acac)$_2$ into another complex. When the sample was allowed to stand for a few days at room temperature, the relative intensities of the spectral lines at the $g_\perp$ component changed slightly. However, as can be seen from Figs. 1 (a) and (b), they altered considerably after the sample had been heated at 100°C and the excess pyridine had been removed. These results show that the formation of the new complex is slow at room temperature, but is accelerated by heating. The spectrum in Fig. 1 (b) consists of many lines with a coupling constant of 16 gauss; this value was determined from the splitting between lines at the central part of the $g_\perp$ component. Figure 1 (c) shows a K-band spectrum in the $g_\perp$ region, which is remarkably broad in contrast to that at the

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1) Y. Yamada, A. Hasegawa, and M. Miura, This Bulletin, **43**, 2661 (1970).

2) H. Yokoi, M. Sai, and T. Isobe, *ibid.*, **43**, 1078 (1970).

3) H. A. Kuska, M. T. Rogers, and R. E. Drullinger, *J. Phys. Chem.*, **71**, 109 (1967).

4) D. P. Graddon, *Nature*, **183**, 1610 (1959).

5) D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, **21**, 49 (1961).

6) A. F. Garito and B. B. Wayland, *J. Amer. Chem. Soc.*, **91**, 866 (1969).

7) T. I. Barry and L. A. Lay, *J. Phys. Chem. Solids*, **27**, 1821 (1966).

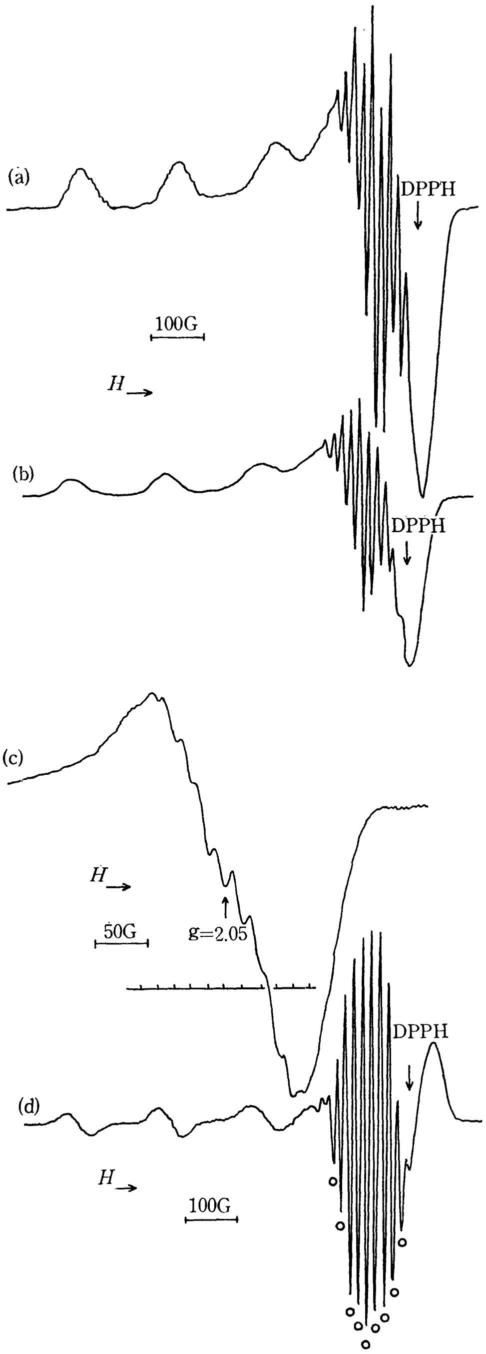

Fig. 1. (a) ESR spectrum of $Cu(acac)_2$ on NaX zeolite in the presence of pyridine at 77°K, (b) spectrum measured at 77°K, after sample (a) was heated at 100°C and excess pyridine was removed, (c) K-band spectrum of sample (a) at 77°K, and (d) second derivative X-band spectrum of sample (b) at 77°K.

X-band. Nevertheless, the observed spectrum consists of lines with a nearly equal splitting of about 16 gauss. Therefore, the separation of $g_\perp$ components, g_x and g_y, due to the deviation from axial symmetry can be disregarded and the value of the coupling constant determined from the X-band spectrum is confirmed.

The superhyperfine (shf) structure arising from the coupling with the nitrogen nucleus of pyridine contributes to the observed spectral lines at the $g_{//}$ component. Therefore, the shf structure should be observed on each of the four lines constituting the parallel hyperfine (hf) structure from the copper atom. Unfortunately, the resolved shf structure in the $g_{//}$ region could not be found, even on the second derivative spectrum (Fig. 1 (d)), but the linewidth of the individual hf structure showed a considerable broadening compared with that for $Cu(acac)_2$ on the zeolite. In a short communication,[1] it has been concluded, on the basis of the 11 lines observed at the $g_\perp$ component, that two of the four oxygen atoms originally coordinating to the cupric ion are replaced by two pyridine molecules. However, an ambiguity remains in this assignment, because the complexity of the spectrum caused by angular anomalies,[8] the electric quadrupole interaction of copper, and the isotope of copper makes it difficult to determine exactly the number of the lines at the $g_\perp$ component. In addition, the number of the lines depends not only on the number of pyridine molecules coordinating to the cupric ion, but also on the ratio of the splitting constant of the copper nucleus to that of the ligand nitrogen nucleus. Since the isotropic hf structure was not observed for this system, it was impossible to determine the perpendicular hf coupling constant of the copper nucleus. Thus, no assignment for the complex can be made. However, the second derivative spectrum shown in Fig. 1 (d) is similar to that for a complex formed in the pyridine - chloroform solution of $CuCl_2$ at 77°K.[9] Moreover, the values of the magnetic parameters obtained from the spectrum of Fig. 1 (b), *i.e.*, $A_{//}$ and $g_{//}$, correspond to those for the complex, in which four pyridine molecules coordinate to the cupric ion in a methanol solution.[10] The intensities of the nine lines at the central part shown in Fig. 1(d) are remarkably stronger than those of the other parts. These lines are represented by circles.

Gersmann and Swalen[9] have reported that the value of the perpendicular hf coupling constant from the copper nucleus is negligibly small in the spectrum observed for $CuCl_2$ in pyridine - chloroform. The same result has also been obtained for $[Cu(pyridine)_4]^{2+}$ in methanol.[10] Hence, assuming that these results can be applied in the present case, the nine intense peaks may be considered to be due only to a shf structure arising from the coupling with four equivalent nitrogen atoms, whereas the weak remaining peaks in the $g_\perp$ region may originate from angular anomalies,[8] the transition with $m_I>0$ due to the electric quadrupole interaction, and the isotopes of copper. These results and considerations lead to the conclusion that the four chelating oxygens of $Cu(acac)_2$ on the zeolite are replaced by four pyridine molecules after the introduction of pyridine, resulting in the formation of a new complex, $[Cu(pyridine)_4]^{2+}$. The substitution reaction was also suggested by the IR measurements; the absorption band at 1580 cm^{-1} for $Cu(acac)_2$ on the zeolite, which has been assigned to the stretching of chelating carbonyl groups,[11] disappears with the adsorption of pyridine.

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[8] L. D. Rollmann and S. I. Chan, *J. Chem. Phys.*, **50**, 3416 (1966).

[9] H. R. Gersmann and J. D. Swalen, *ibid.*, **36**, 3221 (1962).

[10] K. Takimoto, A. Hasegawa, and M. Miura, unpublished results.

[11] R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

TABLE 1. MAGNETIC AND BONDING PARAMETERS OF THE COPMLEXES ON SILICA GEL AND NaX ZEOLITE

	$\lvert A_{//}\rvert\times 10^4\text{cm}^{-1}$	$\lvert A_{\perp}\rvert\times 10^4\text{cm}^{-1}$	$g_{//}$	$g_{\perp}$	α^2	α'^2	β_1^2
Cu(acac)$_2$/SiO$_2$	195	28	2.253	2.055	0.86	0.21	0.72
Cu(acac)$_2$-pyridine/SiO$_2$	166	43	2.311	2.050	0.83	0.24	0.90
Cu(acac)$_2$/NaX zeolite	190	31	2.264	2.043	0.85	0.22	0.75
[Cu(pyridine)$_4$]$^{2+}$/NaX zeolite	196	—	2.254	2.052	0.86	0.22	0.74

The values of the magnetic parameters determined from the spectra of Fig. 1 (b) and of the bonding parameters, calculated using Eqs. (1), (2), and (3) of part I, are listed in Table 1. The observed $|A_{//}|$ value of [Cu(pyridine)$_4$]$^{2+}$ on the zeolite is larger than that of Cu(acac)$_2$. The result can be explained in terms of the fact that the strong coordination of pyridine along the equatorial axis accompanies an increase in covalent character, that is, the promotion of the unpaired electron to the 4s copper orbital, and brings about a positive contribution to the $|A|$ value.[12,13] A similar result has been obtained in the case of copper phthalocyanine[14] or copper tetraphenylporphine,[15] in which the cupric ion is coordinated with four ligand nitrogen atoms. The in-plane σ-bonding of these complexes is known to be highly covalent. Thus, [Cu(pyridine)$_4$]$^{2+}$ is considered to exhibit a considerably covalent character in the copper-nitrogen σ-bonding. However, an unexpected increase in α^2 was obtained (Table 1). This can be interpreted as being caused by the fact that a constant value of κ_0 is used in the calculation of α^2, as has been described in part I.

On the other hand, the value of α'^2 can also be evaluated from the observed shf coupling constant of the nitrogen atoms, independent of the hf coupling constant due to the copper nucleus. The relations between α'^2 and the shf coupling constants are expressed by the following two formulas:[16]

$$A_{\parallel}{}^{\mathrm{N}} = \left(\frac{\alpha'}{4}\right)^2(2\gamma\beta_0\beta_{\mathrm{N}})\left[-\frac{8\pi}{9}|\rho_s(0)|^2+\frac{8}{15}\langle r_p{}^{-3}\rangle\right] \quad (1)$$

$$A_{\perp}{}^{\mathrm{N}} = \left(\frac{\alpha'}{4}\right)^2(2\gamma\beta_0\beta_{\mathrm{N}})\left[-\frac{8\pi}{9}|\rho_s(0)|^2-\frac{1}{15}\langle r_p{}^{-3}\rangle\right] \quad (2)$$

where $A_{//}{}^{\mathrm{N}}$ and $A_{\perp}{}^{\mathrm{N}}$ are the shf coupling constants in the directions of the N–Cu–N axis and perpendicular to it respectively, where $|\rho_s(0)|^2$ is the 2s electron density at the nitrogen nucleus; r_p, the radius of the 2p nitrogen orbital; γ, the gyromagnetic ratio of the ^{14}N nucleus, being set as 0.4036; β_0, the Bohr magneton, and β_{N}, the nuclear magneton. Maki and McGarvey[16] have calculated $|\rho_s(0)|^2=33.4\times10^{24}\text{cm}^{-3}$ for the 2s function and $<r_p{}^{-3}>=21.1\times10^{24}\text{cm}^{-3}$ for the 2p function. By the substitution of the parallel shf coupling constant observed at the $g_{\perp}$ component of the copper, $A_{//}{}^{\mathrm{N}}=15.3\times10^{-4}\text{cm}^{-1}$, into Eq. (1), $\alpha'^2=0.40$ was obtained. Even if the experimental errors are taken into account, this value is still considerably different from that calculated from α^2. This deviation seems to be responsible for the overestimation of α^2 described above. The large parallel shf coupling constant indicates that the copper-nitrogen bond is strong and highly covalent. This result is consistent with that derived from the hf coupling constant of the copper atom.

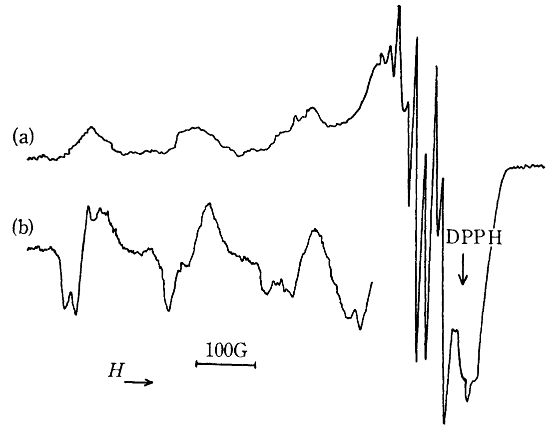

Fig. 2. (a) First and (b) second derivative spectra of Cu(acac)$_2$ on NaX zeolite in the presence of γ-picoline, measured at 77°K after the sample was heated at 80°C.

The Substitution of Cu(acac)$_2$ on the Zeolite with Picoline. When α-, β-, or γ-picoline was used instead of pyridine, the spectra obtained were similar to that observed in the case of pyridine. Figure 2 (a) shows a typical spectrum. The shf structure due to [Cu(picoline)$_4$]$^{2+}$ is also seen on this spectrum, but the intensity ratio of each peak is irregular. The second derivative spectrum in the $g_{//}$ region of Fig. 2 (a) was measured (Fig. 2 (b)). By taking into account the finding that two sets of hf structure are observed in the $g_{//}$ region, two species of the complex are thought to be formed on the zeolite. Hence, it may be deduced that the irregularity is caused by the superposition of the spectra due to the two molecular species. The stability of these complexes lowers in the sequence of γ-, β-, α-picoline; the intensity of the spectrum decreases near 110, 130, and 140°C for the complexes of [Cu(α-picoline)$_4$]$^{2+}$, [Cu(β-picoline)$_4$]$^{2+}$, and [Cu(γ-picoline)$_4$]$^{2+}$ respectively. On the other hand, [Cu(pyridine)$_4$]$^{2+}$ is stable even at 150°C. From these results, the stability of these complexes may be considered to be responsible for the differences in the structure arising from the position of the methyl group and in the interaction with the surface.

The Interaction of Cu(acac)$_2$ with Pyridine on the Various Surfaces. Figures 3, 4, and 5 show the spectra recorded after the introduction of pyridine to Cu(acac)$_2$

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[12] H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, **43**, 1744 (1965).

[13] B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

[14] S. E. Harrison and J. M. Assour, *J. Chem. Phys.*, **40**, 365 (1964).

[15] J. M. Assour, *ibid.*, **43**, 2477 (1965).

[16] A. H. Maki and B. R. McGarvey, *ibid.*, **29**, 35 (1958).

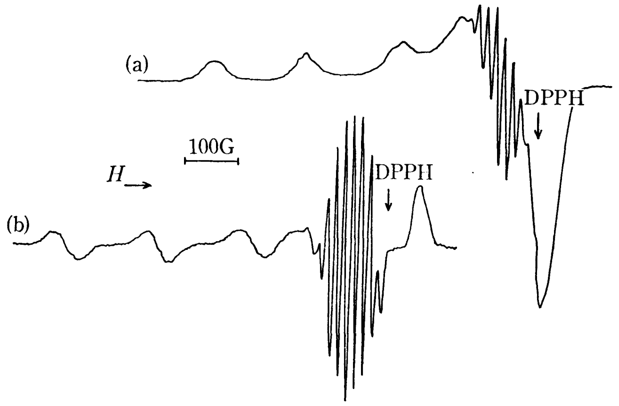

Fig. 3. (a) First and (b) second derivative spectra of [Cu-(pyridine)$_4$]$^{2+}$ on LiX zeolite at 77°K.

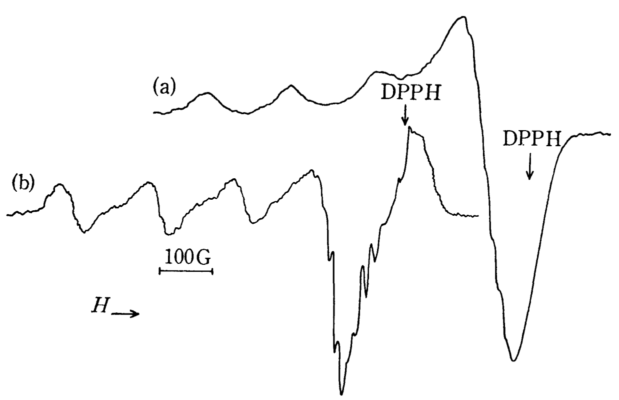

Fig. 4. (a) First and (b) second derivative spectra of [Cu(pyridine)$_4$]$^{2+}$ on NH$_4$X zeolite at 77°K.

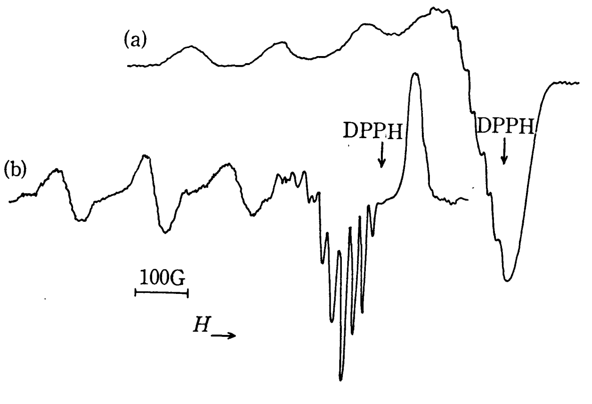

Fig. 5. (a) First and (b) second derivative spectra of [Cu-(pyridine)$_4$]$^{2+}$ on CaX zeolite at 77°K.

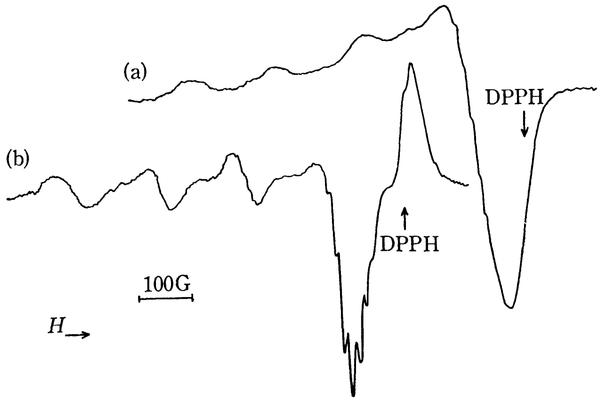

Fig. 6. (a) First and (b) second derivative spectra of [Cu-(pyridine)$_4$]$^{2+}$ on silica-alumina at 77°K.

adsorbed on LiX, NH$_4$X, and CaX zeolites respectively. In the case of LiX zeolite, the shf structure in the $g_\perp$ region is discernible in the first derivative spectrum. On the other hand, for the complex on NH$_4$X or CaX zeolite, the structure is hardly observed in the first derivative because of the linewidth broadening, but it becomes appreciable in the second derivative (Figs. 4 (b) and 5 (b)). All of these spectra have the same shf coupling constant in the $g_\perp$ region as that for the spectrum of [Cu(pyridine)$_4$]$^{2+}$ on NaX zeolite. Therefore, [Cu(pyridine)$_4$]$^{2+}$ must be produced also on these zeolites. Moreover, not only on these zeolites, but on silica-alumina, the formation of [Cu(pyridine)$_4$]$^{2+}$ can be recognized from the second derivative spectrum in Fig. 6 (b).

When Cu(acac)$_2$ on silica gel was exposed to pyridine vapor, a spectrum which is remarkably different from that of [Cu(pyridine)$_4$]$^{2+}$ formed on NaX zeolite appeared, as can be seen in Fig. 7. The magnetic and bonding parameters determined from the spectrum in Fig. 7 are summarized in Table 1. The value of $|A_{//}|$ decreases, but the value of $g_{//}$ increases, in striking contrast to the variation in the parameters of the spectrum observed on NaX zeolite. This means that an adduct is formed, as has been described in part I. Therefore, it can be concluded that such a substitution reaction as observed on the zeolites does not occur on silica gel. This conclusion is predictable from the findings presented in part I; since Cu(acac)$_2$ on silica gel is stable even at 180°C, it is considered that the interaction of quasi-π-electrons in Cu(acac)$_2$ with the surface is weak.

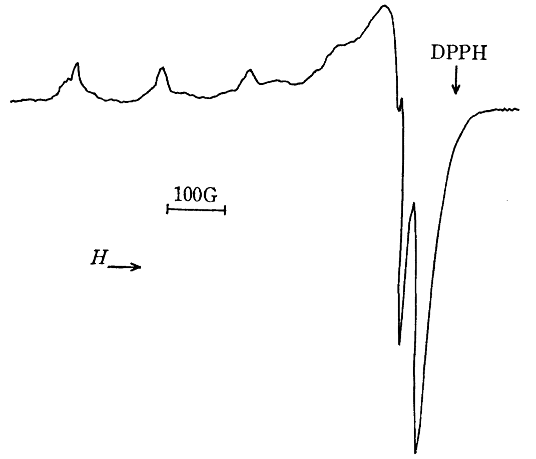

Fig. 7. Spectrum of Cu(acac)$_2$ on silica gel in the presence of pyridine at 77°K.

The Mechanism for the Formation of [Cu(pyridine)$_4$]$^{2+}$. Though the characteristic substitution reaction was not observed in ordinary solvents,[1] the coordination of pyridine along the molecular plane was found in the solution of ethanol - water at pH$\leq$3. It has already been reported that the following reaction takes place in the aqueous ethanol solution at a low pH:[17]

$$\mathrm{Cu(acac)_2} + \mathrm{H^+} \rightleftharpoons [\mathrm{Cu(acac)}]^+ + \text{acetylacetone}$$

Accordingly, the proton may participate also in the substitution reaction on NaX zeolite.

As has been described in part I, the magnetic parameters of the complex on the zeolite are similar to those in toluene. In addition, an IR absorption band due to the stretching of the chelating carbonyl group is observed for $\mathrm{Cu(acac)_2}$ on zeolite. Therefore, it is unnecessary to consider that, before the introduction of pyridine, $\mathrm{Cu(acac)_2}$ dissociates into $\mathrm{Cu^{2+}}$ and two acetylacetone molecules through interaction with NaX zeolite.

Ward[18] has shown, by means of the IR spectra, that NaX zeolite dehydrated fully at 500°C has no detectable Brönsted and Lewis acids, while Watanabe and Habgood[19] have detected the Brönsted acid sites by heating the zeolite under a vacuum at temperatures between 150 and 200°C. Since chloroform contains a trace amount of water,[20] there is a further possibility that the water associated with cation-deficient centers produces the Brönsted-acid sites. Hence, it is thought that the Brönsted-acid sites combine with the adsorbed pyridine molecules to form pyridinium ions. On the other hand, as has been described in part I, the quasi-π-electrons in $\mathrm{Cu(acac)_2}$ interact with the electrostatic field of the cations on zeolites and the complex becomes unstable. Consequently, it can be concluded that two pyridine molecules and two pyridinium ions attack the unstable complex and substitute themselves for the acetylacetone molecules.

When the zeolite was exposed to pyridine vapor and $\mathrm{Cu(acac)_2}$ was then adsorbed on the zeolite, only a faint, broad singlet spectrum was observed, showing that the substitution reaction did not occur. This may be due to the facts that the acid sites are poisoned by the pyridine molecules and that the electrostatic field from the sites is screened. From the results, it seems reasonable to consider that the stability of the complex is not lowered significantly because the interaction of the complex with the zeolite is weakened by the preadsorption of pyridine.

In conclusion, the substitution of the ligands in $\mathrm{Cu(acac)_2}$ with pyridine molecules was found to occur on various zeolites and silica-alumina, but not on silica gel and in ordinary solvents. The complex formed on the zeolites and silica-alumina was identified as $[\mathrm{Cu(pyridine)_4}]^{2+}$ on the basis of the various results and considerations. This reaction was interpreted in terms of both the instabilization of $\mathrm{Cu(acac)_2}$ caused by the interaction of the quasi-π-electrons in $\mathrm{Cu(acac)_2}$ with the electrostatic field of the cations on zeolites, and the attack of two pyridine molecules and two pyridinium ions. Such a substitution reaction was also observed on NaX zeolite using α-, β-, or γ-picoline instead of pyridine, though the complexes produced were less stable than $[\mathrm{Cu(pyridine)_4}]^{2+}$.

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[17] A. H. I. Ben-Bassat and G. Frydman-Kupfer, *Bull. Soc. Chim. Fr.*, **1963**, 2284.

[18] J. W. Ward, *J. Catal.*, **14**, 365 (1969).

[19] Y. Watanabe and H. W. Habgood, *J. Phys. Chem.*, **72**, 3066 (1968).

[20] It was impossible to eliminate completely a trace amount of water from the chloroform.