BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 60—63(1972)

Electron Spin Resonance Studies of Bis(acetylacetonato)copper(II) Adsorbed on X-Type Zeolite. I. Interaction with Ammonia and Aniline

Yoshio YAMADA*

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima

(Received June 7, 1971)

The interaction of bis(acetylacetonato)copper(II) ($Cu(acac)_2$) adsorbed on X-type zeolite of the sodium form and on silica gel with ammonia and aniline was investigated by ESR. The magnetic and bonding parameters for $Cu(acac)_2$ on the surfaces indicate that the axial-ligand field about the copper on the surfaces is similar to that in a toluene solution. This finding implies that the copper in $Cu(acac)_2$ does not interact strongly with these surfaces. However, it was deduced from the change in the spectrum at higher temperatures that the quasi-π-electrons in $Cu(acac)_2$ interact with the electrostatic field arising from the cations on the zeolite. When ammonia or aniline was introduced, the bonding characters of the complex altered significantly. It was found, from the variation in the parameters, that the axial-ligand field about the complex strengthens and that an adduct is formed. Furthermore, a spectral line at $g=2.004$, which was observed only for $Cu(acac)_2$ on the zeolite in the presence of aniline, was considered to be due to a cation radical formed by an electron transfer from the aniline to the complex.

The ESR spectra of copper(II) complexes have been measured in the liquid and frozen solution states by several authors.[1–5] However, very little work has been done as yet on the complexes in the adsorbed state.[6,7] If a copper complex is adsorbed on a solid surface, it can be expected that the interaction of the complex with the surface will alter the bonding character of the complex.

In this paper, the stability of bis(acetylacetonato)-copper(II) in the adsorbed state and the effect of am-

---

* Present address: National Research Institute for Pollution and Resources, Kawaguchi, Saitama, Japan.

[1] D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 149 (1961).

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

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

[4] V. C. Swett and E. P. Dudek, *ibid.*, **72**, 1224 (1968).

[5] K.-E. Falk, E. Ivanova, B. Roos, and T. Vänngard, *Inorg. Chem.*, **9**, 556 (1970).

[6] E. V. Kavalerova, V. B. Golubev, and V. B. Evdokimov, *Zh. Fiz. Khim.*, **37**, 226 (1963).

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

monia or aniline on the adsorbed complex are studied in order to estimate the variation in the bonding character of the complex and in order to examine the interaction with the surface. In the following paper, the reaction of the complex with pyridine will be described on the basis of the interaction with the surface. The purpose of these works is to obtain information on the characteristic reactions taking place on the surface and on the structure of the complex formed on it. In this connection, these studies may contribute to our understanding of heterogeneous catalytic reactions involving complexes.

Experimental

Materials. An X-type zeolite of the sodium form (Linde Lot No. 1380019, Molecular Sieve 13X powder) free from any binder and silica gel was used as the adsorbent. The method of preparation of silica gel has already been described in a preceding paper.[8] The bis(acetylacetonato)-copper(II)($Cu(acac)_2$) was prepared according to the method in the literature[9] and was purified by recrystallization from chloroform. The ammonia and aniline were repeatedly distilled under a vacuum prior to use. The former was synthesized by the ordinary method, while the latter was obtained commercially.

Procedures. The zeolite was heated in a vacuum for 5 hr at 500°C. The amount of $Cu(acac)_2$ (0.88 mg in 1 m*l* of chloroform per 0.25 g of the zeolite) was adjusted so that all of the complex molecules entered the cages of the zeolite in the ratio of one molecule to *ca.* 20 cages. The chloroform solution of $Cu(acac)_2$ was introduced to the zeolite through a breakable seal. Note should be taken of the procedure that the zeolite was cooled before the introduction of the solution in order to prevent the $Cu(acac)_2$ from decomposing by the heat of adsorption. After the chloroform had been eliminated under a vacuum, the complex adsorbed on the zeolite was exposed, at room temperature, to ammonia at a pressure of 100 Torr or to aniline vapor, and then the ESR spectra were measured with a Japan Electron Optics Laboratory JES-3BS-X type ESR spectrometer, equipped with a 100kc field-modulation unit. The g value was determined by comparison with the value for DPPH, 2.0036.

Results and Discussion

The ESR spectrum of $Cu(acac)_2$ adsorbed on the X-type zeolite is shown in Fig. 1 (a). It can be considered, from the well-resolved lines of this spectrum, that the complex molecules are sufficiently remote from one another. When a Molecular Sieve 3A was used as the adsorbent, only a broad singlet spectrum was observed. The absence of structure seems to be ascribable to the dipole-dipole interaction among the complex molecules. From the difference between these spectra, the complex molecules may be deduced to be included in the cages of the X-type zeolite.

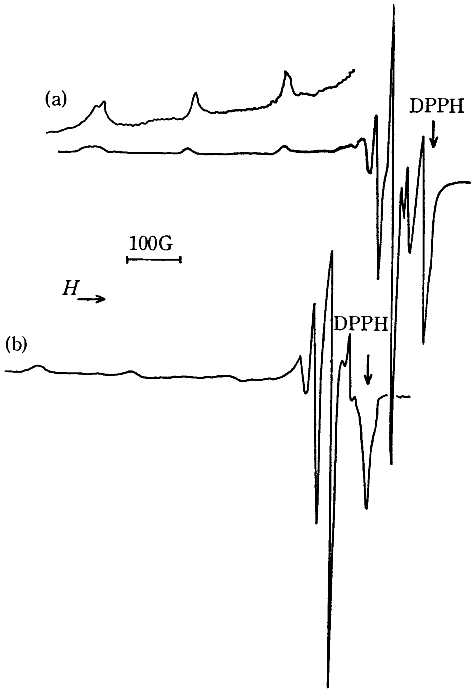

Fig. 1. ESR spectra of $Cu(acac)_2$ (a) on NaX zeolite and (b) on silica gel at 77°K.

If the complex takes a structure with a completely axial symmetry, the spectrum at the perpendicular g component ($g_\perp$) should consist of four lines as a result of the coupling between an electron spin and a nuclear moment ($I=3/2$) of copper, neglecting the isotope of its nucleus.[10] However, a few unexpected peaks, which had also been observed in the frozen solution,[2] were found, as can be seen in Fig. 1 (a). Recently, these extra peaks have been analyzed on the basis of a theoretical consideration.[11] According to this theory, the observed peaks seem to be due not only to the separation of $g_\perp$ components, g_x and g_y, because of the deviation from axial symmetry, but also to angular anomalies and to transitions with $m_I>0$ caused by electric quadrupole effects.

When the complex was adsorbed on silica gel, a spectrum similar to that on the zeolite was observed

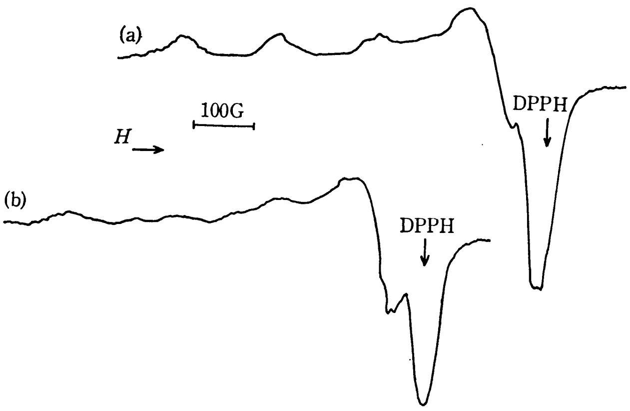

Fig. 2. Spectra of $Cu(acac)_2$ (a) on NaX zeolite and (b) on silica gel in the presence of ammonia (100 Torr) at 77°K.

---

[8] M. Miura, A. Hasegawa, and Y. Yamada, *ibid.*, **41**, 1320 (1968).

[9] M. M. Jones, *J. Amer. Chem. Soc.*, **81**, 3188 (1959).

[10] The maximum separation due to copper nuclei (^{63}Cu and ^{65}Cu) is about 2—3 gauss at the $g_\perp$ component.

[11] L. D. Rollmann and S. I. Chan, *J. Chem. Phys.*, **50**, 3416 (1969).

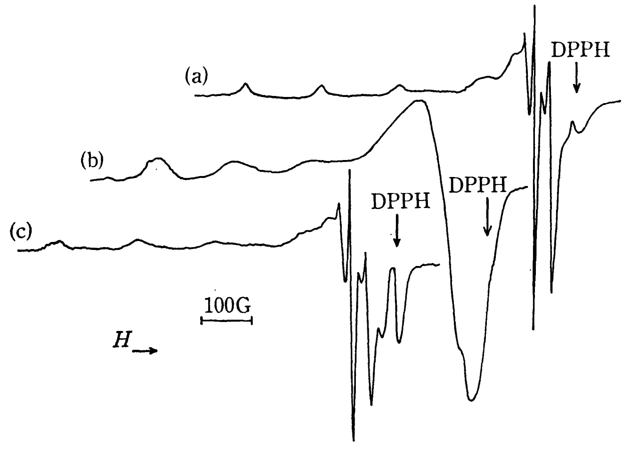

Fig. 3. Spectra of Cu(acac)$_2$ (a) on NaX zeolite (b) on silica gel in the presence of aniline at 77°K, and (c) 77°K after sample (a) was left for a few days at room temperature.

(Fig. 1 (b)). The extra peaks in the $g_\perp$ region are not clearly discernible, as may be seen in Fig. 1 (b), because of the linewidth broadening. The spectra shown in Figs. 2 (a) and (b) were obtained when ammonia was introduced, at a pressure of 100 Torr, to Cu(acac)$_2$ on the zeolite and the silica gel respectively, and then the samples were heated at 80°C. The original spectrum was replaced by an ill-resolved one in each case. On the other hand, the well-resolved spectrum shown in Fig. 3 (a) appeared on the exposure of the Cu(acac)$_2$ on the zeolite to aniline vapor. A weak singlet at g=2.004 behaved differently from the other signals in the variation of the temperature and the microwave power. A detailed discussion of the singlet will be presented later. The magnetic parameters determined from these spectra are listed in Table 1, along with those from the spectrum of Cu(acac)$_2$ in a toluene solution.12)

In order to discuss the nature of the copper-ligand bonding in terms of these experimental parameters, the bonding parameters were calculated by a molecular orbital theory.1,13) That is, α^2, which is a measure of the covalency of in-plane σ-bonding between a copper 3d orbital and the ligand orbitals, can be written in the first approximation:

$$A_{\parallel} = P\left[-\alpha^2\left(\frac{4}{7}+\kappa_0\right)+(g_{\parallel}-2.002) + \frac{3}{7}(g_\perp-2.002)+0.04\right] \quad (1)$$

where P=0.036 cm^{-1} and where κ_0 is the Fermi contact term for the free cupric ion and is nearly equal to 0.43, according to Kivelson and Neiman.1)

The value of β_1^2, which is a measure of the covalency of the in-plane π-bonding, was evaluated from the equation:

$$g_{\parallel} - 2.002 = -8\rho[\alpha\beta_1-\alpha'\beta_1 S-\alpha'(1-\beta_1^2)^{1/2}T(n)/2] \quad (2)$$

where $\rho=\lambda_0\alpha\beta_1/\Delta E_{xy}$ and where $T(n)$ has the value of 0.220 for the β-keto enolate chelates. The spin-orbit coupling constant for the free cupric ion, λ_0, is −828 cm^{-1}. On account of the difficulty in observing the absorption spectra, the energy difference between E_{xy} and $E_{x^2-y^2}$ is approximately set as the constant value of 15000 cm^{-1}. The normalization of the in-plane σ-bonding orbital yields:

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha' S = 1, \quad (3)$$

where S, the overlap integral, is equal to 0.076 for the β-keto enolate complexes. By the use of Eqs. (1), (2), and (3), the values of the bonding parameters, that is, α^2, β_1^2, and α'^2, were calculated; the results are summarized in Table 2.

TABLE 1. MAGNETIC PARAMETERS

	$g_{\parallel}$	$g_\perp$	$\lvert A_{\parallel}\rvert\times 10^4$cm^{-1}	$\lvert A_\perp\rvert\times 10^4$cm^{-1}
Cu(acac)$_2$ in $C_6H_5CH_3$ a)	2.246	2.062	197	15
Cu(acac)$_2$ on SiO$_2$	2.253	2.055	195	28
Cu(acac)$_2$ on zeolite	2.264	2.043	190	31
Cu(acac)$_2$ on SiO$_2$–NH$_3$	2.240	2.029	193	— b)
Cu(acac)$_2$ on zeolite–NH$_3$	2.268	2.034	183	— b)
Cu(acac)$_2$ on SiO$_2$–$C_6H_5NH_2$	2.301	2.031	160	— b)
Cu(acac)$_2$ on zeolite–$C_6H_5NH_2$	2.300	2.054	165	23

a) Ref. 12
b) These values were not obtained.

TABLE 2. BONDING PARAMETERS

	α^2	α'^2	β_1^2
Cu(acac)$_2$ in $C_6H_5CH_3$	0.82	0.25	0.73
Cu(acac)$_2$ on SiO$_2$	0.86	0.21	0.72
Cu(acac)$_2$ on zeolite	0.85	0.22	0.75
Cu(acac)$_2$ on SiO$_2$–NH$_3$	0.83	0.24	0.71
Cu(acac)$_2$ on zeolite–NH$_3$	0.83	0.24	0.79
Cu(acac)$_2$ on SiO$_2$–$C_6H_5NH_2$	0.80	0.27	0.91
Cu(acac)$_2$ on zeolite–$C_6H_5NH_2$	0.82	0.25	0.89

Prior to the consideration of the bonding character, the stability of the complex on the surfaces was examined. The intensity of the spectrum of Cu(acac)$_2$ adsorbed on the zeolite gradually decreased and the linewidth became broader as the temperature was raised. The spectrum disappeared near 90°C. The broadening of the spectral lines can be explained in terms of the decomposition of the complex; the cupric ion thus produced interacts more strongly with the surface than that in the complex does. On the other hand, a small decrease in the intensity was observed up to *ca.* 200°C for Cu(acac)$_2$ on silica gel. It, therefore, may be considered that the especially active sites on the zeolite play an important role in the decomposition of the complex. Abramov *et al.*14) studied the IR spectra of benzene adsorbed on zeolites and interpreted the various shifts of some bands in the IR spectra as being caused by the interaction of the π-electron of the benzene molecule with the electrostatic field of the cations on the walls of the cavities in the zeolites. An

---

12) S. Antosik, N. M. D. Brown, A. A. McConnell, and A. L. Porte, *J. Chem. Soc.*, A, **1969**, 545.

13) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 31 (1958).

14) V. N. Abramov, A. V. Kiselev, and V. I. Lygin, *Zh. Fiz. Khim.*, **37**, 1156 (1963).

essentially similar interaction can be expected for the quasi-π-electrons in Cu(acac)$_2$ adsorbed on the zeolite. As can be seen in Table 2, the in-plane π-bonding for Cu(acac)$_2$ on the zeolite is somewhat more ionic than that for the complex on silica gel. This may be interpreted as follows: the symmetry of the complex lowers slightly as a result of the interaction of the quasi-π-electrons in the complex with the electrostatic field from the cations on the zeolite, and the copper atom is no longer coplanar to the four chelating oxygen atoms.

It is well known that the magnetic parameters of copper complexes depend largely upon the kind of solvent.[12] This arises from the differences in the basicity of the solvent molecules, one or two of which coordinate to the complex along the axis normal to the molecular plane. When apical ligands coordinate to the cupric ion, *i.e.*, when the axial-ligand field strengthens, the values of $g_{//}$ increase, while those of $|A_{//}|$ decrease.[5,15] On the basis of this rule and the results shown in Table 1, the axial field can be said to be weak in the adsorbed state as well as in a toluene solution, where none of the solvent molecules coordinates to the complex as an apical ligand.[12] Consequently, it seems reasonable to consider that the copper atom in the complex does not interact strongly with the surface.

When ammonia or aniline is introduced to Cu(acac)$_2$ on the zeolite or silica gel, the $g_{//}$ value increases and the $|A_{//}|$ value decreases, except for Cu(acac)$_2$ on silica gel in the presence of ammonia. According to the above rule, these facts may indicate that the adsorbed molecule coordinates as an apical ligand. Since such basic molecules have a strong donating ability, their equatorial coordination should be weakened by back-donation, resulting in an increase in α^2. Nevertheless, this phenomenon was not seen on the introduction of ammonia or aniline. This unexpected result may be attributable to the use of the Fermi contact term, κ_0, as a constant in the calculations. It has been indicated[16] that the axial coordination of the electron-donating molecule increases the charge density in the 4*s* orbital, thereby reducing the promotion of the unpaired electron to the 4*s* orbital and causing a decrease in κ_0. Hence, this conflict can be removed in terms of the decrease in κ_0. From the above discussion, it can be concluded that the introduction of aniline or ammonia to Cu(acac)$_2$ on the zeolite, and that of aniline to Cu(acac)$_2$ on silica gel, bring about the axial-ligand field, leading to the formation of the adduct, though the circumstances of the complex are not clear for the system of Cu(acac)$_2$-ammonia on silica gel. Furthermore, when we take into account the finding that the copper atom in the complex interacts more strongly with ammonia or aniline than with the surface, it seems likely that the complex has such a structure that the copper atom is located above the plane containing the four chelating oxygen atoms. These oxygen atoms may interact with the surface hydroxy groups.

When Cu(acac)$_2$ adsorbed on the zeolite in the presence of aniline was allowed to stand for a few days at room temperature, the spectral line at g=2.004 in Fig. 3 (a) grew considerably, whereas the other lines arising from the complex slightly decayed (Fig. 3 (c)). The saturation curves for microwave power of the former line and of the latter lines were recorded according to the methods described by Bloembergen and Wang.[17] It was found from the curves that the former line easily saturates with microwave power. These results suggest that there is a possibility of the formation of a cation radical by the electron transfer from aniline to Cu(acac)$_2$. The ionization potential of aniline, which was measured by the photoionization method, is 7.7 eV.[18] This value is quite low.

When the temperature of the system was raised, the intensity of the signal due to the cation radical increased remarkably and became constant near 130°C. From the increase in the radical concentration, it may be deduced that the mixing of the lone-pair orbital with an orbital of the copper atom occurs to a greater extent as a result of the strong interaction between the copper atom and the aniline molecule at elevated temperatures, and that it accelerates the electron transfer. The formation of radical was observed in the solution containing aniline.

The effect of the zeolite on aniline in the absence of Cu(acac)$_2$ was examined in an additional experiment. When aniline was adsorbed on the zeolite, a weak line, probably due to the cation radical, was observed at the same position as above, but its intensity did not increase at higher temperatures. It can be concluded from these facts that the cation radical formed in the system of Cu(acac)$_2$-aniline on the zeolite arises mainly from the electron transfer and partly from some other mechanism.

The author wishes to express his hearty thanks to Professor Masaji Miura and Dr. Akinori Hasegawa for their valuable discussions and encouragement throughout this work.

---

[15] H. Yokoi, M. Sai, and T. Isobe, This Bulletin, **42**, 2232 (1969).

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

[17] N. Bloembergen and S. Wang, *Phys. Rev.*, **93**, 72 (1954).

[18] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).