The Substitution Reaction of Ligands in Copper(II) Acetylacetonate with Pyridine on a Molecular Sieve 13X

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It has been reported that well-resolved hyperfine structures of ESR spectra are obtained for copper(II) acetylacetonate (Cu(acac)$_2$) on silica gel.$^{1)}$ The present authors found that the complex also presents a distinct ESR spectrum on a Molecular Sieve 13 X (MS). In this paper, it will be reported that the substitution of a part of the ligands in Cu(acac)$_2$ with pyridine is observed on the MS surface, but not in solutions containing pyridine.

The MS powder (Linde Lot No. 1380019) was treated in a vacuum for 5 hr at 500°C. The amount of Cu(acac)$_2$ used as the adsorbate was adjusted so as to be included in the cages of the MS in the ratio of one molecule to 20 cages. The solution of Cu(acac)$_2$ in chloroform was outgassed and introduced to the MS through a breakable seal. After the chloroform had been eliminated by means of a vacuum line, the complex adsorbed on the MS was exposed to pyridine vapor at room temperature and the ESR spectrum was measured at 77°K.

The spectral lines of perpendicular *g* components for the Cu(acac)$_2$ on MS were replaced upon the adsorption of pyridine by those consisting of about 11 lines, with a splitting of 16 gauss, as is shown in Fig. 1. The latter spectral lines can be explained by supposing that, in addition to the hyperfine splitting due to the copper nucleus, there exists a superhyperfine structure arising from ligand nitrogen atoms. On the other hand, none of the superhyperfine structure due to the ligand nitrogen atoms was observed in Cu(acac)$_2$ dissolved in 60% pyridine - 40% chloroform, 60% pyridine - 40% methanol, or 25% pyridine-25% water-50% methanol at 77°K.$^{2)}$ Moreover, no ESR signal was obtained upon the adsorption of pyridine alone on MS. These results may imply that some of the ligands of the complex are substituted on the MS with pyridine molecules, but not in the solution containing pyridine. This conclusion is supported by the IR measurements; the absorption band at 1580 cm^{-1} of Cu(acac)$_2$ on MS, which has been assigned to the stretching of chelated carbonyl groups, disappears in Cu(acac)$_2$-pyridine on MS. The formation of Cu(pyridine)$_4{}^{2+}$ is not possible since the idea of a charge transfer during the substitution with pyridine is unreasonable. Consequently, the spectral lines exhibited in Fig. 1 seems to be due to the signal of a new complex in which two of four oxygen atoms originally coordinated with copper are replaced by two nitrogen atoms of pyridine. The observed spectral lines can be satisfactorily explained by the assumption that the ratio of the splitting constant of the copper nucleus to that of two ligand nitrogen atoms is 2 : 1 and that the separation of perpendicular *g* components can be disregarded.[*1] A spectrum similar to that of Cu(acac)$_2$-pyridine on MS was observed when 4-methylpyridine was used instead of pyridine. It can be deduced from these results that such a characteristic substitution reaction is caused by the excitation of Cu(acac)$_2$ arising from the interaction of the complex with the active site on MS.

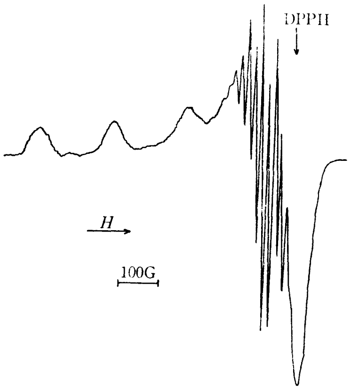

Fig. 1. ESR spectrum of Cu(acac)$_2$ on MS in the presence of pyridine at 77°K.

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1) E. V. Kavalerova, V. B. Golubev and V. B. Evdokimov, *Zhur. Fiz. Khim.*, **37**, 226 (1963).

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

[*1] This was confirmed by means of a K-band ESR spectrometer.