CHEMISTRY LETTERS, pp. 477-478, 1974. Published by the Chemical Society of Japan

ESR STUDY OF THE INTERACTION OF BIS(ACETYLACETONATO)COPPER(II) WITH HETEROCYCLES

Tamizo KOGANE, Haruo YUKAWA, and Reiko HIROTA*
Industrial Research Institute of Kanagawa Prefecture, 3173
Showa-cho, Kanazawa-ku, Yokohama 236
* Faculty of Science, Rikkyo University, Nishi-ikebukuro,
Toshima-ku, Tokyo 171

From ESR spectra measurements we report that bis(acetylacetonato)copper(II) forms 1:2 adduct with weak Lewis bases containing oxygen or nitrogen.

Bis(β-diketonato)copper(II) chelates have planar monomeric structures in solution, and usually have the ability to form coordination bonds with either one or two molecules of Lewis bases in the axial positions.$^{1)}$ It has been reported that bis(hexafluoroacetylacetonato)copper(II)$^{2,3)}$ and bis(trifluoroacetylacetonato)copper(II)$^{4)}$, which are stronger Lewis acids than bis(acetylacetonato)copper(II)(Cu(acac)$_2$), form stable 1:1 and 1:2 adducts with pyridine, whereas Cu(acac)$_2$ forms unstable adducts.$^{5)}$

We have investigated the interaction of Cu(acac)$_2$ with weak Lewis bases by ESR, and observed that Cu(acac)$_2$ forms 1:1 and 1:2 adducts in chloroform solution with heterocycles containing oxygen and nitrogen.

The ESR spectra of Cu(acac)$_2$ were measured in frozen chloroform solution containing 70% or higher concentrations of various heterocycles. The concentration of Cu(acac)$_2$ used was 1.0×10^{-2}M.

All the ESR spectra of Cu(acac)$_2$ solution with low heterocycle concentrations exhibited only signals assigned to 1:1 adduct formation. At higher heterocycle concentrations the spectrum of the solution showed a new signal on the lower field side of the signal corresponding to 1:1 adduct. An example of the ESR spectra of Cu(acac)$_2$ in chloroform-heterocyclic ligands solution is shown in Fig. 1. As long as the samples were kept in a dark place below 0°C, spectra were appreciably reproducible. However, when the sample solution was diluted with

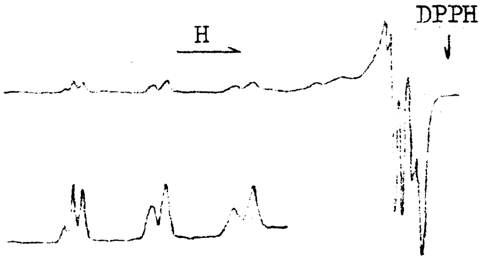

Fig. 1. ESR spectra of Cu(acac)$_2$ in 80% pyridine-20% chloroform at 113°K.

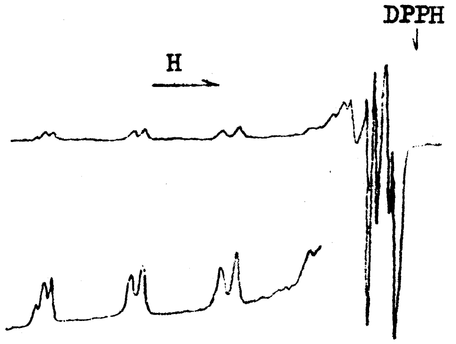

Fig. 2. ESR spectra of $Cu(acac)_2$ in 70% tetrahydrofuran-30% chloroform at 113°K.

Table 1. ESR parameters.

Compounds	1:1 adduct $g_{\parallel}$	$\lvert A_{\parallel}\rvert$ ($\times 10^4 cm^{-1}$)	1:2 adduct $g_{\parallel}$	$\lvert A_{\parallel}\rvert$ ($\times 10^4 cm^{-1}$)
4-Ethylpyridine	2.292	163	2.323	149
Pyridine	2.290	165	2.317	152
Pyradine	2.280	172	2.305	159
Tetrahydrofuran	2.274	176	2.293	168
Tetrahydropyran	2.271	178	2.291	170
2,5-Dihydrofuran	2.272	179	2.297	167

chloroform, disappearance of the second signal was observed. Since the ESR spectrum for the $Cu(acac)_2$-pyridine complex exhibits no resolvable ^{14}N hyperfine splitting, the second complex is not expected to have the structure of square pyramidal type with the heterocyclic nitrogen occupying a basal plane.$^{6)}$ Higher $g_{\parallel}$ values and lower $|A_{\parallel}|$ values than those of 1:1 adducts are observed, and they are attributed to 1:2 adducts of $Cu(acac)_2$ with pyridine bases.$^{7)}$

The ESR spectra of $Cu(acac)_2$ in higher concentration of tetrahydrofuran are shown in Fig. 2. The $g_{\parallel}$ vs. $|A_{\parallel}|$ plot for each of these two series gives a straight line, and it means that the heterocycles containing oxygen form 1:2 adducts with $Cu(acac)_2$ as well as pyridine bases (Table 1). Such an interaction for the formation of 1:1 and 1:2 adducts increases as the basicity of the solvents becomes larger.

REFERENCES

1) D. P. Graddon, Coord. Chem. Rev., 4, 1 (1969).
2) W. R. Walker and N. C. Li, J. Inorg. Nuclear Chem., 27, 2255 (1965).
3) N. C. Li, S. M. Wang, and W. R. Walker, ibid., 27, 2263 (1965).
4) R. D. Gillard and G. Wilkinson, J. Chem. Soc., 1963, 5885.
5) D. P. Graddon and E. C. Watton, J. Inorg. Nuclear Chem., 21, 49 (1961).
6) B. B. Wayland and M. D. Wisniewski, Chem. Commun., 1971, 1025.
7) S. Antosik, N. M. D. Brown, A. A. McConnell, and A. L. Porte, J. Chem. Soc. (A), 545 (1969).

(Received February 28, 1974)