The Reaction of Bis(2-cyanopyridine)copper(II) Chloride with Amines in Methanol

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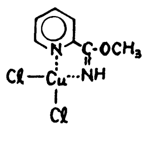
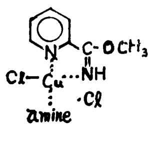
It has been reported [1] that 2-cyanopyridine is alcoholized with transition metal ions (*e.g.* Cu(II), Ni(II) and Co(II)) in alcohols to afford complexes of *O*-alkyl pyridine-2-carboximidate, Type I. It is assumed that the nitrile group of 2-cyanopyridine is activated by chelation with the metal ion and therefore the attack of the nucleophiles (*e.g.* OR^- or OH^-[2]) on it is promoted. To develop this idea, a test of amination to the nitrile group in chelates was made with various amines. We obtained not the expected complexes but new ones (Types II and III).

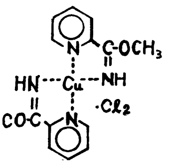
When ammonia, methylamine, dimethylamine, ethylamine, or benzylamine was used for the reaction, the chelates of Type II were obtained. On the other hand, when trimethylamine, diethylamine, or triethylamine was used, only the chelate of Type III was obtained. The methanol solution of bis(2-cyanopyridine)copper(II) chloride[1] and that of amines (1—2 mol to the complex) were mixed at 0°C and the reaction mixture was stirred for 45—60 min. The precipitate of the complex was then obtained by addition of ether, and was recrystallized from methanol-ether mixture at room temperature.



(MeOpy)$CuCl_2$
(I)[1]



(MeOpy)(amine)$CuCl_2$
(II)



$(MeOpy)_2CuCl_2$
(III)

The results of elementary analysis and spectroscopic measurements of the chelates are given in Tables 1 and 2. In Table 1, the chelates of Type II are 1)—5). The chelate of Type III is 6). The ultraviolet and the visible spectra of 6) differ from those of the chelates of Type II, which suggests the structural difference between the chelates of these two types. The formation of the chelate of Type III seems to be due to the steric hindrance of bulky alkyl groups in the amines.

TABLE 1. ANALYTICAL DATA OF COMPLEXES

Compound	No.	Cu, % Found	Cu, % Calcd	C, % Found	C, % Calcd	H, % Found	H, % Calcd	N, % Found	N, % Calcd
$(MeOpy)(NH_3)CuCl_2$	1)	22.56	22.09	29.07	29.23	3.75	3.86	14.59	14.61
$(MeOpy)(CH_3NH_2)CuCl_2$	2)	21.06	21.06	32.07	31.85	4.32	4.35	13.40	13.93
$(MeOpy)[(CH_3)_2NH]CuCl_2$	3)	19.95	20.13	34.24	34.24	4.58	4.80	13.07	13.31
$(MeOpy)(CH_3CH_2NH_2)CuCl_2$	4)	19.9	20.13	34.33	34.24	4.85	4.80	13.20	13.31
$(MeOpy)(\langle\bigcirc\rangle CH_2NH_2)CuCl_2$	5)	16.70	16.82	44.35	44.51	4.32	4.54	11.18	11.13
$(MeOpy)_2CuCl_2$	6)	15.72	15.62	40.67	41.33	4.06	3.97	13.33	13.78

TABLE 2. COLOR, ABSORPTION MAXIMA AND INFRARED ABSORPTION MAXIMA OF COMPLEXES

No.	Color	ν_{max} max in cm^{-1} and log ε (in parentheses) in methanol		C–N str.	C–O–C (cm^{-1}) antisym. str.
1)	pale blue	36600 (3.85)	14900 (1.89)	1655	1388
2)	blue green	36600 (3.85)	14700 (1.93)	1646	1382
3)	light green	36600 (3.85)	14600 (1.92)	1644	1386
4)	blue green	36600 (3.85)	15000 (1.85)	1646	1385
5)	deep blue	36600 (3.85)	14600 (1.95)	1655	1381
6)	pale blue	36600 (4.06)	12900 (2.02)	1646	1398

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1) P. F. B. Barnard, *J. Chem. Soc.*, *A*, **1969**, 2140.

2) K. Sakai, T. Ito, and K. Watanabe, This Bulletin, **40**, 1660, (1967).