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The Reaction of Bis(2-pyridinecarbonitrile)copper(II) Chloride with Methanol and Various Amines

Shinnichiro Suzuki,[1] Masayoshi Nakahara,* and Ken-ichi Watanabe

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo 158

**Department of Chemistry, Faculty of Science, Rikkyo University, Nishi-ikebukuro, Toshima, Tokyo 171*

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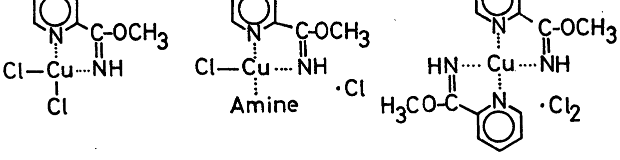
On treatment of bis(2-pyridinecarbonitrile)copper(II) chloride with various amines in methanol, the alkoxylation of the nitrile group in the complex took place; in some cases, the alkoxylation and the ligand substitution of the complex occurred at the same time. The reaction products were classified into three types depending on the amines used; two of the types consisted of new complexes. The complexes of $CuCl_2(MeOpy)(Amine)$ (MeOpy: *O*-methylpyridine-2-carboximidate), were obtained on the addition of ammonia, methylamine, dimethylamine, ethylamine, benzylamine, or piperidine to a methanol solution of bis(2-pyridinecarbonitrile)copper(II) chloride. On the other hand, the addition of trimethylamine, diethylamine, or triethylamine afforded the complex of $CuCl_2(MeOpy)_2$. These types of complexes were not obtained by the use of aniline or pyridine; but the previously known complex, $CuCl_2(MeOpy)$, was obatined in this case. It has been assumed that the formation of the three types of complexes is essentially the result of both the basicities and the steric factors of the amines.

It has been reported that 2-pyridinecarbonitrile readily gives the chelates of 2-pyridinecarboxamide or *O*-methylpyridine-2-carboximidate(MeOpy) upon heating with transition-metal ions, *e.g.*, Cu(II) or Ni(II), in water[2,3] or methanol[3] respectively. Although 2-pyridinecarbonitrile coordinates *via* the nitrogen atom of the pyridine ring to the metal ions, the nitrile group in the 2-position is presumed to have an interaction with the metal ions and to be easily attacked by the nucleophilic reagents, water or alcohols.

The amination of the nitrile group in $PtCl_2(CH_3CN)_2$ has been reported by Stephenson.[4] We tried the addition of amines to bis(2-pyridinecarbonitrile)copper(II) chloride in methanol. However, no amination products but the following three types of copper(II) complexes were obtained (Fig. 1); the complexes of Type II and III were new ones. A brief note has been already reported.[5] In this paper, the relationship between the cause of the formation of the different types of complexes and their structures will be discussed.



$CuCl_2(MeOpy)$, Type I; $CuCl_2(MeOpy)(Amine)$, Type II; $CuCl_2(MeOpy)_2$, Type III

Fig. 1. Three types of copper(II) complexes.

Experimental

Preparation of Bis(2-pyridinecarbonitrile)copper(II) Chloride. Commercial 2-pyridinecarbonitrile was purified by recrystallization from ether; mp 26.5—27.5 °C. A dry methanol solution of 2-pyridinecarbonitrile(2 mol) was added to a dry methanol solution of copper(II) chloride dihydrate (1 mol) at 0 °C. The mixture was stirred vigorously to yield deep blue crystals. The crystals were immediately collected by filtration, and washed with ether. They were then dried over phosphorus pentoxide *in vacuo*. Found: C, 42.04; H, 2.48; N, 15.99; Cu, 18.45% Calcd for $CuCl_2(C_5H_4NCN)_2$: C, 42.06; H, 2.36; N, 16.35; Cu, 18.54%.

Reaction of Bis(2-pyridinecarbonitrile)copper(II) Chloride with Methanol and Various Amines. Bis(2-pyridinecarbonirile)-copper(II) chloride was suspended by stirring it in dry methanol at 0 °C, and then a methanol solution of an amine (1 or 2 mol) was immediately added to it. After the mixture had been stirred for 45—60 min at 0 °C, ether was added until bluish green crystals were precipitated; these crystals were then separated by filtration. They were instantly washed with ether several times and dried over silica gel *in vacuo*. All the products were obtained quantitatively. For recrystallization, the precipitates were dissolved in methanol, and ether was added until fine crystals were deposited. Since the recrystallization of ethylamine complex was not easy, its methanol solution was kept overnight at room temperature. The various complexes thus obtained are shown in Table 1, while the analytical data of the new complexes are given in Table 2.

$CuCl_2(NH_3)(MeOpy)$–No. 2– was also synthesized by means of the following method. At room temperature, ammonia gas was bubbled into 50 ml of a methanol solution containing 1.0 g of $CuCl_2(MeOpy)$, No. 1. The reaction occurred immediately, and the color of the reaction mixture changed from bluish green to violet. Then the reaction mixture was concentrated to about 15 ml. The violet precipitates of the tetraamminecopper (II) chloride which had been initially deposited were filtered off, and pale blue $CuCl_2(NH_3)$-(MeOpy), crystals were obtained by adding ether to the filtrate. It was recrystallized from methanol ether mixture three times.

Instraments. The electronic and infrared spectra were obtained with Hitachi Recording Spectrophotometers, ESP-3T and EPI-G-2 respectively.

Results and Discussion

Absorption Spectra. The absorption spectra of the complexes synthesized are listed in Table 3. All the copper(II) complexes have d-d bands in the 12900—15000 cm^{-1}, $\log \varepsilon = 1.8$—2.0, while the bands of $\log \varepsilon = 3.85$ in the ultraviolet region (36600 cm^{-1}) are mainly due to the pyridine ring in the ligand. As for the infrared spectra of all the complexes, the bands of the

TABLE 1. REACTION PRODUCTS OF BIS(2-PYRIDINECARBONITRILE)COPPER(II) CHLORIDE AND VARIOUS AMINES IN METHANOL

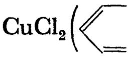
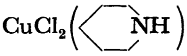
Type	Compound No.	Amine	pK_a	Products	Color
I	1	Aniline Pyridine	4.60 5.18	$CuCl_2(MeOpy)$	Bluish green
II	2	Ammonia	9.25	$CuCl_2(NH_3)(MeOpy)$	Pale blue
	3	Methylamine	10.62	$CuCl_2(CH_3NH_2)(MeOpy)$	Bluish green
	4	Dimethylamine	10.77	$CuCl_2(CH_3)_2NH(MeOpy)$	Light green
	5	Ethylamine	10.63	$CuCl_2(CH_3CH_2NH_2)(MeOpy)$	Bluish green
	6	Benzylamine	9.35	$CuCl_2$(-CH_2NH_2)(MeOpy)	Deep blue
	7	Piperidine	11.12	$CuCl_2$()(MeOpy)	Light green
III	8	Trimethylamine Diethylamine Triethylamine	9.80 10.93 10.87	$CuCl_2(MeOpy)_2$	Pale blue

TABLE 2. ANALYTICAL DATA OF COMPLEXES

Compound No.	Formula	Cu(%)		C(%)		H(%)		N(%)	
		Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
2	$CuCl_2C_7H_{11}ON_3$	22.56	22.09	29.07	29.23	3.75	3.86	14.59	14.61
3	$CuCl_2C_8H_{13}ON_3$	21.06	21.06	32.07	31.85	4.32	4.35	13.40	13.93
4	$CuCl_2C_9H_{15}ON_3$	19.95	20.13	34.24	34.24	4.58	4.80	13.07	13.31
5	$CuCl_2C_9H_{15}ON_3$	19.9	20.13	34.33	34.24	4.85	4.80	13.20	13.31
6	$CuCl_2C_{14}H_{17}ON_3$	16.70	16.82	44.35	44.51	4.32	4.54	11.18	11.13
7	$CuCl_2C_{12}H_{19}ON_3$	17.81	17.86	40.34	40.51	5.10	5.39	11.44	11.81
8	$CuCl_2C_{14}H_{16}O_2N_4$	15.72	15.62	40.67	41.33	4.06	3.97	13.33	13.78

TABLE 3. ABSORPTION MAXIMA IN VISIBLE, ULTRAVIOLET AND INFRARED REGION

No.	ν_{max} in cm^{-1} and log ε (in parentheses, ε = molar extinction coefficient) in methanol		C=N (cm^{-1})	C–O–C (cm^{-1})
1	13300 (1.81)	36600 (3.85)	1658[a)]	1380[a)]
2	14900 (1.89)	36600 (3.85)	1655	1388
3	14700 (1.93)	36600 (3.85)	1646	1382
4	14600 (1.92)	36600 (3.85)	1644	1386
5	15000 (1.85)	36600 (3.85)	1646	1385
6	14600 (1.95)	36600 (3.85)	1655	1381
7	14600 (1.87)	36600 (3.83)	1647	1388
8	12900 (2.02)	36600 (4.06)	1646	1398

a) Ref. 2.

N–H stretching vibrations of amines or of the imidate group appeared at 3000—3300 cm^{-1}. The C–N stretching and antisymmetric C–O–C stretching vibrations of the imidate group appeared at about 1650 and 1380 cm^{-1} respectively.

The Formation of the Type I Complex. The complex of Type I, which is prepared by heating equimolar amounts of 2-pyridinecarbonitrile and copper(II) chloride in methanol, has already been reported by Barnard.[3)] In our studies, it was also prepared easily when aniline or pyridine was added to a methanol solution containing an equimolar amount of bis(2-pyridinecarbonitrile)copper(II) chloride. However, by adding an excess of amine —but less than two moles—, a mixture of the Type I complex and the copper(II) complex of aniline or pyridine was obtained.

The Formation of the Type II Complexes. The complexes of Type II (Nos. 2—7, Table 1) were obtained by adding amines to a methanol solution of bis(2-pyridinecarbonitrile)copper(II) chloride. The amines used are shown in Table 1. The amount of amines employed was 1—2 mol for bis(2-pyridinecarbonitrile)copper(II) chloride. On the contrary, each aminecopper(II) complex was formed by employing more than two moles of amines. The difference in the composition of the Type II complexes from that of the other types is observed in the absorption spectra data (d-d bands, λ_{max} = 14600—15000 cm^{-1}) in Table 3. In particular, the d-d band of No. 2 (Type II) was shifted to the range of shorter wavelengths and increased in its absorption intensity as compared with that of No. 1. This indicates the coordination of ammonia in the No. 2. From the infrared spectral data in Table 3, the bands of C–N stretching vibrations of the imino group (Nos. 2—7) are known to be shifted to the range of lower wave numbers than that of the Type I complex (1658 cm^{-1}). Accordingly, it is presumed that these shifts may be attributed to the coordination of various amines in the complexes.

The Formation of the Type III Complexes. The addition of trimethylamine, diethylamine, or triethylamine to bis(2-pyridinecarbonitrile)copper(II) chloride in methanol always afforded a complex of Type III, $CuCl_2(MeOpy)_2$. With regard to the ultraviolet absorption bands due to the ligand, MeOpy (in Table 3), the absorption intensity of No. 8 is about twice that of No. 1, hence, No. 8 obviously contains two molecules of MeOpy.

The Effect of Amines. It was concluded that 2-pyridinecarbonitrile coordinated to the copper(II) ion underwent alkoxylation and/or ligand-exchange reaction in the presence of various amines. However, the complex formations of the different types, from I to III, are mainly dependent on the basicities and steric factors of the amines used.

In the case of Type I complex formation, in the presence of a weaker base, such as aniline or pyridine, the interaction of the amine with the metal ion is not strong enough to form a mixed-ligand complex such as Type II. However, when a large excess of the amine was employed, only an amine complex was obtained by the ligand exchange (*e.g.* an aniline or pyridine copper-(II) complex).

It is conceivable that the distinction between the formation of Types II and III complexes is due mainly to steric effects between amines and the MeOpy group. The basicities of the amines belonging to Types II and III are similar (Table 1, pK_a). The amines which afford the complexes of Type II have little steric hindrance and easily coordinate to the metal ion by means of the ligand exchange. On the other hand, the amines which have bulky alkyl groups, *e.g.*, trimethylamine, diethylamine, and triethylamine, do not afford amine complexes by the steric hindrance; they only act as catalysts for the alkoxylation (Type III). In order to prepare a Type III complex without amines, it is necessary for the reaction mixture to be refluxed more than 5 hr.

Reference and Footnote

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