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NEW COPPER(I) COMPLEXES CONTAINING p-BENZOQUINONE AS LIGAND

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A deep green Cu(II) complex, $[\mathrm{CuPyCl(OCH_3)}]_n$ (A) has been reported by Finkbeiner et al who prepared it by oxygen oxidation of copper(I) chloride in a methanol-pyridine mixture or by treating copper(II) chloride in methanol solution with 1 equivalent of sodium methoxide and then adding pyridine to the reaction mixture (1). We have found that a new Cu(I) complex (B) containing p-benzoquinone is obtained as reddish orange precipitate when the complex (A) is reacted with hydroquinone in a o-dichlorobenzene-methanol mixture under nitrogen atmosphere. The complex (B) had the composition of $\mathrm{Cu_2Py_2Cl_2(C_6H_4O_2)}$, was considerably stable when dry and could be stored in vacuum desiccator at room temperature (Anal. Calcd. for $\mathrm{C_{16}H_{14}Cl_2N_2O_2Cu_2}$: C, 41.39 ; H, 3.04 ; N, 6.03 ; Cl, 15.27, Cu, 27.37. Found : C, 40.53 ; H, 3.24 ; N, 5.95 ; Cl, 15.0 ; Cu, 27.8). It liberated p-benzoquinone on thermal decomposition. The infra red spectrum of the complex (B) showed the characteristic bands of pyridine at 1607, 1444, 759, 691 $\mathrm{cm^{-1}}$ etc and the bands of p-benzoquinone at 1658, 1642, 861 $\mathrm{cm^{-1}}$ etc. While the far infra red spectrum of the complex (A) showed one band at 536 $\mathrm{cm^{-1}}$ assigned to streching frequency of $\mathrm{Cu{-}OCH_3}$, this band disappeared in the complex (B). Therefore, it may be concluded that the complex (B) contains pyridine and benzoquinone ligands but does not contain methoxide ligands.

The complex (B) absorbed 0.5 mol of oxygen in methanol based on

1 mol of $Cu_2Py_2Cl_2(C_6H_4O_2)$ to convert to the complex (A). At high dilution, the green solution of the complex (A) in methanol was obtained and this solution was treated again with hydroquinone under nitrogen atmosphere to reproduce the precipitate of the complex (B). In this case, to reproduce the complex (B) quantitatively from the solution, at least 0.5 mol of hydroquinone per atom of copper in the complex (A) was required, showing that the ratio of copper atom to benzoquinone molecule in the complex (B) is probably 2 : 1. Benzoquinone ligand in the complex (B) could not be replaced with pyridine in benzene at a room temperature but could be easily replaced with triphenylphosphine in benzene to produce a triphenylphosphine-containing copper complex which was not examined further.

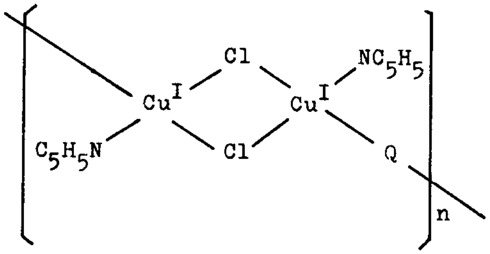
ESR measurement of the complex (B) showed neither the presence of any organic free radical and nor the signal of Cu(II). While the complex (A) had the effective magnetic moment, μeff of 0.69, the complex (B) was diamagnetic (Table 1). From the above results, all coppers in the complex (B) are concluded to be in Cu(I) state.

TABLE 1

Effective Magnetic Moment of Some Copper Complexes

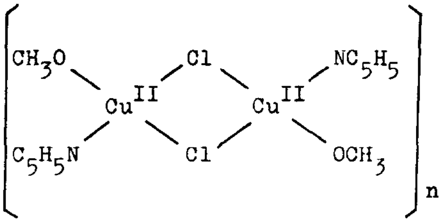
Cu Complex	Composition	μ eff
(A)	$CuPyCl(OCH_3)$	0.69
(A')	$CuPcCl(OCH_3)$	0.48
(A'')	$CuLCl(OCH_3)$	0.57
(B)	$Cu_2Py_2Cl_2(C_6H_4O_2)$	diamagnetic
(B')	$Cu_2Pc_2Cl_2(C_6H_4O_2)$	diamagnetic
	$CuCl(OCH_3)$	1.87
	$Cu(OCH_3)_2$	1.12
	$CuPy_2Cl_2$	2.00

A deep green Cu(II) complex, $[\mathrm{CuPcCl(OCH_3)}]_n$ (A') and a olive green Cu(II) complex, $[\mathrm{CuLCl(OCH_3)}]_n$ (A'') in which Pc and L represent 2-picoline and 2,6-lutidine, were prepared by using 2-picoline and 2,6-lutidine respectively in place of pyridine in a similar manner to the preparation of the complex (A). With the use of 2,2'-bipyridyl, Cu(II) complex of A-type could not be isolated in a pure state under the similar conditions. The complex (A') and (A'') had μeff of 0.48 and 0.57 respectively. A new orange Cu(I) complex was obtained from the complex (A') but a similar Cu(I) complex was not obtained from the complex (A'') under the same conditions as those of preparation of the complex (B). The complex (B') had the composition of $\mathrm{Cu_2Pc_2Cl_2(C_6H_4O_2)}$ and was diamagnetic (Anal. Calcd. for $\mathrm{C_{18}H_{18}Cl_2N_2O_2Cu_2}$: C, 43.91 ; H, 3.69 ; N, 5.69 ; Cl, 14.40 ; Cu, 25.81, Found : C, 43.69 ; H, 3.66 ; N, 5.37 ; Cl, 14.9 ; Cu 26.7). The complex (B') appears to be less stable than the complex (B). Therefore, abilities as ligand to stabilize Cu(I) complex of B-type decrease in the order of Py $>$ Pc $>$ L. As the order is reverse to basicities of the ligands, stabilities of the B-type complexes seem to be considerably affected with steric effects of the ligands. From all results described above, we propose the structure of the Cu(I) complex (B) as I :

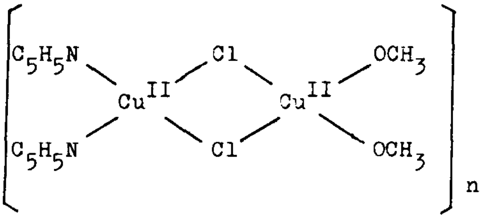


(I)

where Q represents benzoquinone molecule. The mode of bonding between copper atom and benzoquinone molecule can not be deduced from these experiments. Moreover, it is reasonable to consider that the parent Cu(II) complex (A) has the structure of II rather than that of III which was proposed previously (1).



(II)



(III)

Such symmetrical configuration of methoxide ligands as II is also compatible with the fact that the far infra red spectral band due to streching of Cu-OCH_3 is a singlet, because it may be expected for the less symmetrical structure III that the band shows a doublet.

REFERENCE

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