# *Some Copper Complexes of Diazoaminobenzene Derivatives and their Properties**

By Hiraku YAMADA, Hiroshi OHTA, Masaru YAMAGUCHI and Tokuichi TSUMAKI

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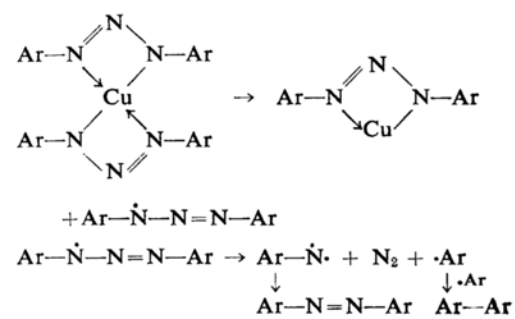
It is well known that the copper(I) complexes of diazoaminobenzene and its derivatives are, in some organic solvents, more stable than the copper(II) complexes. Dwyer et al.[1-6] found that in solution the copper(II) complex of diazoaminobenzene decomposed rapidly into the copper(I) complex by auto-reduction, splitting off the organic fragments. But they did not investigate these fragment. In the present paper are described the synthesis of the copper(II) complexes of diazoaminobenzene derivatives and the isolation and identification of their thermal decomposition products.

As the starting materials for the synthesis of the copper(II) complexes, we chose 4, 4'-dichloro-, 4, 4'-dimethoxy-, 4-chloro-, 4-methoxy- and 4-ethoxydiazoaminobenzenes. The synthesis of their copper(II) complexes was fairly difficult owing to their extreme instability in solution. The synthesis was, therefore, carried out successfully at low temperature, and, in some cases, at temperature as low as possible by cooling with an ethanol-dry ice bath. The complexes were obtained as dark green crystals or powder. In the dry state they are stable, but in solution they become much less stable; and, when heated, they decompose very rapidly into black brown solutions containing tarry substances.

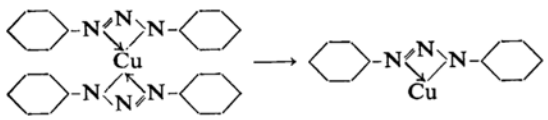
From the tarry substances we could obtain by chromatography on alumina, the copper(I) complexes as yellow to orange-red crystals. From the solution after the separation of the copper(I) complexes a considerable amount of azobenzene derivatives was obtained.

In order to obtain some knowledge concerning the decompositon mechanism, we furthermore investigated the thermal decomposition products of bis(diazoaminobenzene)copper(II) [or bis(1, 3-diphenyltriazenato)copper(II)] and estimated quantitatively nitrogen gas evolved by the thermal decomposition of the copper(II) complexes of diazoaminobenzene derivatives. From bis(diazoaminobenzene)copper(II), only biphenyl, not azobenzene, was obtained. Further it was ascertained that one molecule of nitrogen was evolved per molecule of each of the complexes during the decomposition. It is, therefore, considered most probable that the decomposition of the copper(II) complexes proceeds in the manner shown below.



* "Co-ordinate Valency Rings" XXIX. XXVIII of this series: Y. Kihara, H. Ohta and T. Tsumaki, *Mem. Faculty Sci., Kyushu Univ., Ser. C, Chem.*, **3**, 137 (1960).

1) F. P. Dwyer, *J. Soc. Chem. Ind.*, **58**, 110 (1939); *Chem. Abstr.*, 33. 5818 (1939).
2) F. P. Dwyer, *Australian Chem. Inst. J. and Proc.*, **6**, 348 (1939); *Chem. Abstr.*, **34**, 733 (1940).
3) F. P. Dwyer, ibid., **6**, 362 (1939); *Chem. Abstr.*, **34**, 734 (1940).
4) F. P. Dwyer, *J. Am. Chem. Soc.*, **63**, 79 (1941).
5) F. P. Dwyer et al., ibid., **63**, 81 (1941).
6) F. P. Dwyer et al., *Chemistry and Industry*, **1940**, 136; *Chem. Abstr.*, **34**, 3245 (1940).



## Experimental

The following diazoaminobenzene derivatives were synthesized:

4,4'-dichlorodiazoaminobenzene[7],
4,4'-dimethoxydiazoaminobenzene[8],
4,4'-diethoxydiazoaminobenzene[9],
4-chlorodiazoaminobenzene[10],
4-methoxydiazoaminobenzene[11],
and 4-ethoxydiazoaminobenzene[12]

**The Synthesis of the Copper(II) Complexes of Diazoaminobenzene Derivatives.**—*General Remarks*: Since the copper(II) complexes of diazoaminobenzene and its derivatives are very unstable in solution, the synthesis must always be carried out below 0°C.

**Bis(4, 4'-dichlorodiazoaminobenzene)copper(II).**—To a solution of 5 g. of 4,4'-dichlorodiazoaminobenzene in 50 cc. of ethanol is added a solution of 1.8 g. of copper acetate in 100 cc. of the same solvent. The solvent is removed in vacuo, till the precipitate deposits. The precipitate is filtered off and washed with water and then with ethanol. The precipitate is then dissolved in cold acetone and concentrated under reduced pressure at room temperature, when dark green crystals separate out. Dark green plates, which decompose violently at 114°C. Soluble in acetone, ethanol, benzene and chloroform.

Found: C, 48.02; H, 3.02; N, 18.18; Cu, 11.43. Calcd. for $C_{24}H_{16}N_6Cl_4Cu$: C, 48.54; H, 2.72; N, 14.15; Cu, 10.70%.

**Bis(4, 4' - dimethoxydiazoaminobenzene)copper(II).**—To a solution of 5.2 g. of 4,4'-dimethoxydiazoaminobenzene in 100 cc. of ether is added a solution of 1.8 g. of copper acetate in 200 cc. of ethanol, and the mixture is cooled in an ethanol-dry ice bath and stirred well. The color of the solution becomes green. After standing for an hour, the solvent is removed under reduced pressure at room temperature. The precipitate produced is filtered and washed successively with water, ethanol, acetone and ether, and dried. Dark green micro-crystals, which decompose at 200~204°C. Soluble in acetone, ethanol, benzene and chloroform. In solution it is extremely unstable.

Found: C, 58.45; H, 5.08; N, 14.47; Cu, 11.08. Calcd. for $C_{28}H_{28}N_6O_4Cu$: C, 58.37; H, 4.90; N, 14.59; Cu, 11.03%.

**Bis(4, 4'-diethoxydiazoaminobenzene)copper(II).**—To a solution of 5.7 g. of 4,4'-diethoxydiazoaminobenzene in 200 cc. of acetone is added a solution of 1.8 g. of copper acetate in 100 cc. of ethanol, and the mixture is maintained between −10~−20°C for an hour, and after that concentrated under reduced pressure. The precipitate is filtered and washed successively with water, acetone and ether, and dried. Dark green plates, which decompose at 150°C. Soluble in ether, acetone and ethanol.

Found: C, 60.28; H, 6.05; N, 13.20; Cu, 9.92. Calcd. for $C_{32}H_{36}N_6O_4Cu$: C, 60.79; H, 5.74; N, 13.29; Cu, 10.05%.

**Bis(4-chlorodiazoaminobenzene)copper(II).**—To a solution of 4.5 g. of 4-chlorodiazoaminobenzene in 100 cc. of ethanol is added a solution of 1.8 g. of copper acetate in 100 cc. of ethanol, and the mixture is maintained between −10~−20°C for an hour, and then concentrated under reduced pressure at room temperature. The precipitate is filtered, washed successively with water, ethanol, and ether, and dried. Dark green powder, which decomposes at 85~87°C. Soluble in acetone, ethanol and benzene.

Found: C, 57.07; H, 3.84; N, 15.97; Cu, 12.05. Calcd. for $C_{24}H_{18}N_6Cl_2Cu$: C, 54.92; H, 3.46; N, 16.01; Cu, 12.10%.

**Thermal Decomposition of the Copper(II) Complexes of Diazoaminobenzene Derivatives in Solution.**—One per cent solution of each of the copper(II) complexes in acetone, benzene or ether is refluxed on a water-bath. In 15~30 min. the color of the solution changes from green to black-brown, and a tarry precipitate is produced. After 1~3 hr. the decomposition is complete. The tarry precipitate is filtered off from the solution, dissolved in benzene-chloroform-petroleum ether mixture and chromatographed on alumina, when the copper(I) complexes were obtained. The effluent was combined with the filtrate from the tarry precipitate and the combined solution was used for the later operations.

The following copper(I) complexes were obtained.

**4, 4' - Dichlorodiazoaminobenzenecopper(I).**—Yellow needles, which decompose at 242°C explosively. Readily soluble in benzene and chloroform, soluble with difficulty in ether and acetone.

Found: C, 43,47; H, 2.46; N, 12.20; Cu, 19.34. Calcd. for $C_{12}H_8N_3Cl_2Cu$: C, 43.85; H, 2.45; N, 12.78; Cu, 19.33%.

**4, 4' - Dimethoxydiazoaminobenzenecopper(I).**—Orange-red needles, which decompose at 228°C, giving tarry substance. Readily soluble in benzene and chloroform, soluble with difficulty in ether and acetone.

Found: C, 52.95; H, 4.56; N, 13.88; Cu, 19.78. Calcd. for $C_{14}H_{14}N_3O_2Cu$: C, 52.58; H, 4.41; N, 13.14; Cu, 19.87%.

**4, 4'-Diethoxydiazoaminobenzenecopper(I).**—Orange-colored needles, which decompose at 240°C, giving tar. Readily soluble in benzene and ethanol, soluble with difficulty in ether and acetone.

Found: C, 55.59; H, 5.55; N, 12.01; Cu, 18.12. Calcd. for $C_{16}H_{18}N_3O_2Cu$: C, 55.24; H, 5.22; N, 12.08; Cu, 18.26%.

The above-mentioned combined solution was extracted with 1 N hydrochloric acid after the addition of 3~4 times its volume of ether. From this acid extract no identifiable substance was obtained. The remaining ether solution was chromatographed on alumina, using petroleum ether, petroleum benzine and acetone as eluents, when

7) R. Meldola et al., *J. Chem. Soc.*, **53**, 670 (1888).
8) M. Busch and E. Bergmann, *Chem. Zentr.*, **1905 I**, 1102.
9) R. Henriques, *Ber.*, **25**, 3064 (1892).
10) A. Hantzsch et al., ibid., **30**, 1413 (1897).
11) D. Vorländer, ibid., **62**, 2830 (1929).
12) D. Vorländer, ibid., **62**, 2825 (1929).

five fractions were obtained. From the first fraction the following azobenzene derivatives were obtained, and identified by the measurement of the mixed melting point with the authentic samples: 4,4'-dichloroazobenzene, 4,4'-dimethoxyazobenzene, and 4,4'-diethoxyazobenzene. From the fractions following we could not obtain any identifiable substances. We could, further, obtain biphenyl from the decomposition products of bis(diazoaminobenzene)copper(II) in benzene, but in this case we could not notice azobenzene.

**Determination of Nitrogen Gas Evolved during the Decomposition of the Copper(II) Complexes in Solution.**—The solution of 20~25 mg. of the complex in 10 cc. of benzene was heated in an airtight vessel in a stream of carbon dioxide. After removal of benzene vapour through the efficient trap cooled by dry ice, the nitrogen gas evolved was collected on an azotometer. The results are shown below:

| Copper(II) complexes (one mole) | Nitrogen gas evolved (mole) |
|---|---|
| Bis(4, 4'-dichlorodiazoaminobenzene)copper(II) | 0.754 |
| Bis(4, 4'-dimethoxydiazoaminobenzene)copper(II) | 0.952 |
| Bis(4, 4'-diethoxydiazoaminobenzene)copper(II) | 0.836 |
| Bis(4-chlorodiazoaminobenzene)-copper(II) | 0.748 |

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*Department of Chemistry*
*Faculty of Science*
*Kyushu University*
*Hakozaki, Fukuoka*