

BINUCLEAR METAL COMPLEXES. V.¹⁾ TEMPLATE SYNTHESIS OF A BINUCLEAR
COPPER(II) COMPLEX OF A MACROCYCLE CONTAINING AMIDO GROUPS

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A new binucleating ligand, 2,6-bis(β-aminoethylcarbamoyl)-4-methylphenol was prepared and its copper(II) complex was isolated. By the reaction of this complex and 2,6-diformyl-4-methylphenol, a binuclear copper(II) complex of a new macrocycle, 23,24-dihydroxy-10,21-dimethyl-3,6,14,17-tetraazatricyclo[17,3,1,1^{8,12}]tetracos-1(23),6,8(24),9,11,13,19,21-octaene-2,18-dione, was synthesized.

It is well known that 2,6-diformyl-4-methylphenol²⁾ and its Schiff bases²⁻⁶⁾ form binuclear copper(II) complexes, where the phenolic oxygen acts as a bridge. Since a diamido-derivative of 4-methylphenol-2,6-dicarboxylic acid is similar to these ligands in structure, it may also form binuclear copper(II) complex.

We prepared a new binucleating ligand, 2,6-bis(β-aminoethylcarbamoyl)-4-methylphenol (1), and its copper(II) complex (2). When the complex (2) and 2,6-diformyl-4-methylphenol were treated in DMF, a binuclear copper(II) complex (3) of a macrocycle, 23,24-dihydroxy-10,21-dimethyl-3,6,14,17-tetraazatricyclo[17,3,1,1^{8,12}]tetracos-1(23),6,8(24),9,11,13,19,21-octaene-2,18-dione, was obtained (Fig. 1).

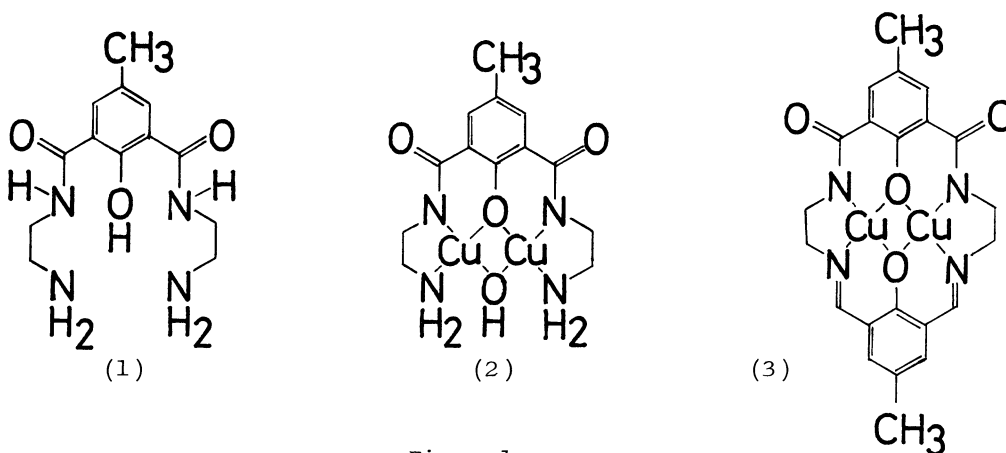


Fig. 1.

A few binucleating⁷⁻¹⁰⁾ and many mononucleating macrocyclic ligands have been synthesized by the template action of metal ions. Most binucleating macrocycles⁷⁻⁹⁾

have been made by the direct reaction of a carbonyl compound and a diamine in a presence of a metal ion. Recently Okawa and Kida¹⁰⁾ prepared some macrocycles, that are capable of forming binuclear complexes, by the unique reaction of free carbonyl groups in a coordinated complex and a diamine. The template reaction in the present research is novel in that the macrocycle was formed by the reaction of the coordinated amino groups and the polydentate carbonyl compound, where the reaction centers are considerably separated from each other. It should be also noticed that the hydroxy bridging group was exchanged with the phenolic oxygen during the cyclization reaction.

The synthetic scheme of the ligand is shown in Fig. 2. A powdered mixture of 2,6-diethyl-4-methylphenol (10 g) and potassium hydroxide (50 g) was heated at 230°C on an oil-bath for 1 hour. The evolution of hydrogen gas was observed during this reaction. The reaction mixture was poured into water and acidified with hydrochloric acid to give a white precipitate. 4-Methylphenol-2,6-dicarboxylic acid, crystallized

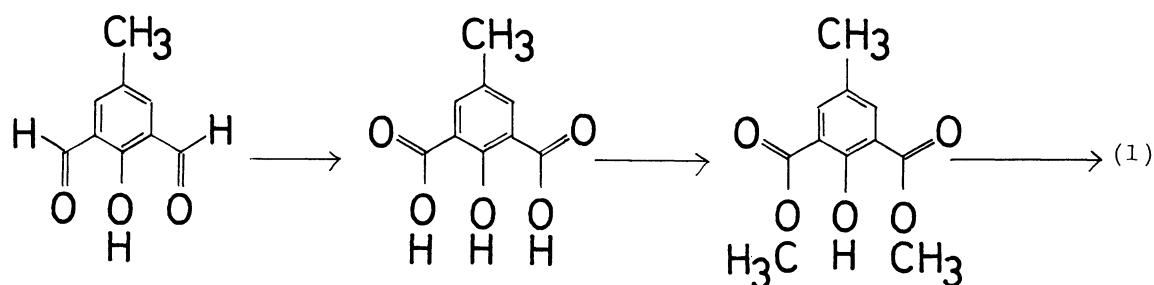


Fig. 2. Synthetic scheme of the ligand.

from ethanol, melts at 234°C. Found: C, 55.54; H, 4.38%. Calcd for $C_9H_8O_5$: C, 55.11; H, 4.11%. The dicarboxylic acid (5 g), methanol (10 ml), sulfuric acid (0.75 ml) and dichloromethane (15 ml) were refluxed for 7 hours. The reaction mixture was extracted with benzene, washed with water, 10%-sodium bicarbonate solution and then with water. The white precipitate, which was obtained by evaporating the solvent, was crystallized from methanol, to give white needles of dimethyl 4-methylphenol-2,6-dicarboxylate, which melts at 121-122°C. Found: C, 58.44; H, 5.29%. Calcd for $C_{11}H_{12}O_5$: C, 58.93; H, 5.39%. The diester (2.5 g) and a large amount of ethylenediamine were mixed in methanol and allowed to stand for 1 day at room temperature. Methanol and excess of ethylenediamine were evaporated under reduced pressure to give a pale yellow, oily substance, which is supposed to be the compound (1). The IR spectrum of the compound shows no absorption band due to ester group but shows the

C=O stretching vibration of amido group at 1550 cm^{-1} and the N-H stretching vibration of the amido and amino groups in the region of $3000\text{--}3300\text{ cm}^{-1}$. This ligand was used for the preparation of the complex (2) without further purification.

The ligand (1) and copper(II) perchlorate hexahydrate (1:2 mole ratio) were dissolved in water. To this solution was added an aqueous solution of two equivalent of sodium hydroxide to give blue-violet prisms. Found: C, 34.19; H, 4.99; N, 12.24; Cu, 13.65%. Calcd for $\text{C}_{13}\text{H}_{18}\text{N}_4\text{O}_4\text{Cu}_2 \cdot 2\text{H}_2\text{O}$: C, 34.14; H, 4.85; N, 12.25; Cu, 13.89%. It is insoluble in most solvents. The IR spectrum of the complex exhibits the C=O vibration of amido group at 1530 cm^{-1} and the N-H vibrations at 3290 and 3250 cm^{-1} . The sharp band at 3510 cm^{-1} may be assigned to the O-H stretching vibration of the bridging group. The visible spectrum on a powder shows a d-d band around 17.1 kK . The magnetic moment at room temperature is 1.14 B.M. , that is markedly smaller than the "spin-only value" 1.73 B.M. , suggesting an antiferromagnetic exchange interaction between the copper(II) ions. The ESR spectrum (X-band) on a powder at 153°K shows two signals; a broad band (1700 gauss width) centered at 3200 gauss and a very weak signal at 1590 gauss . These might be assigned to the $\Delta M_s = 1$ and $\Delta M_s = 2$ transitions respectively. From these facts it was concluded that the complex possesses the structure (2) given in Fig. 1.

To a boiling suspension of the complex (2) in DMF, a solution of an equimolar amount of 2,6-diformyl-4-methylphenol in DMF was dropwise added, and the mixture was refluxed for 5 hours. During this time blue-violet prisms disappeared and orange prisms deposited. Found: C, 48.13; H, 4.01; N, 10.36%. Calcd for $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_4\text{Cu}_2 \cdot \text{H}_2\text{O}$: C, 48.09; H, 4.04; N, 10.20%. It was also insoluble in most solvents. In the IR spectrum of the complex the absorption bands due to the amino and hydroxy groups were not observed and a new band was found at 1625 cm^{-1} , which was attributed to the C=N stretching vibration. The reflectance spectrum on a powder shows a d-d band at 18.0 kK . The magnetic moment at room temperature was found to be 0.79 B.M. . From these facts we concluded that the complex has the binuclear structure (3) of the macrocycle.

Amino nitrogen coordinated to a metal ion is usually inert for nucleophilic attack. However an inductive effect of copper(II) ions in the complex (2) may accelerate the deprotonation at the terminal nitrogens. The $\text{--}\overset{\ominus}{\text{N}}\text{H}(\rightarrow\text{Cu})$ group thus formed will easily attack the carbonyl carbon of 2,6-diformyl-4-methylphenol, and the thermodynamically stable complex (3) with the 6-6-5-6-6-5 condensed ring system

will be finally formed. In going from the complex (2) to the complex (3), the energy of the d-d band increases and the magnetic moment decreases. These facts imply that the planar configuration around the copper(II) ions in the complex (3) is sufficiently strengthened by the rigid skeleton constructed with the macrocyclic moiety. The same trend in d-d band and effective magnetic moment has been found for the binuclear copper(II) complexes of pyridine-N-oxides¹¹⁾ and N-aryl-salicylaldimines.¹²⁾

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