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*Syntheses and Properties of 2'-Amino-4'-methylbiphenyl-2-ol
and Its Copper(II) Complexes*

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Synopsis: A new bidentate ligand, 2'-amino-4'-methylbiphenyl-2-ol (Hambp), was synthesized. An examination of its behavior toward metal ions proved that, depending on the reaction conditions, the ligand gave mononuclear or polynuclear copper (II) complexes with seven-membered chelate rings. The complexes of the following compositions were thus characterized: $[\text{Cu}(\text{ambp})_2(\text{Hambp})] \cdot 1/4\text{H}_2\text{O}$, $\text{Cu}_5(\text{ambp})_8(\text{OH})_2$ and $\text{Cu}_2(\text{ambp})_3(\text{OH}) \cdot \text{CH}_3\text{COOC}_2\text{H}_5 \cdot \text{H}_2\text{O}$.

In the previous paper¹⁾, syntheses and properties of 2'-aminobiphenyl-2-ol and its copper(II) complexes were reported. As an extension of the previous work, 2'-amino-4'-methylbiphenyl-2-ol, a methyl derivative of 2'-aminobiphenyl-2-ol¹⁾, was synthesized according to the scheme in Fig. 1 and the formation and the properties of its copper(II) complexes were studied.

The dissolving-metal reduction of 2-methoxy-2'-nitro-4'-methylbiphenyl(I) with Raney alloy led to 2-amino-4-methyl-2'-methoxybiphenyl(2), which was then demethylated with boiling hydrobromic acid giving Hambp(3) in a fair yield.

When the ligand was treated with copper(II) ions in an ammoniacal aqueous ethanolic solution, the hexa-coordinated mononuclear complex of the composition, $[\text{Cu}(\text{ambp})_2(\text{Hambp})] \cdot 1/4\text{H}_2\text{O}$ (abbreviated as Com-Cu), was obtained in the form of dark brown needles. The complex gave polynuclear $\text{Cu}_5(\text{ambp})_8(\text{OH})_2$ (abbreviated as Com- Cu_5) when heated with benzene, and $\text{Cu}_2(\text{ambp})_3(\text{OH}) \cdot \text{CH}_3\text{COOC}_2\text{H}_5 \cdot \text{H}_2\text{O}$ (abbreviated as Com- Cu_2) when heated with ethyl acetate. The examination of the IR, UV and magnetic susceptibilities supported the above conclusion as will be discussed below.

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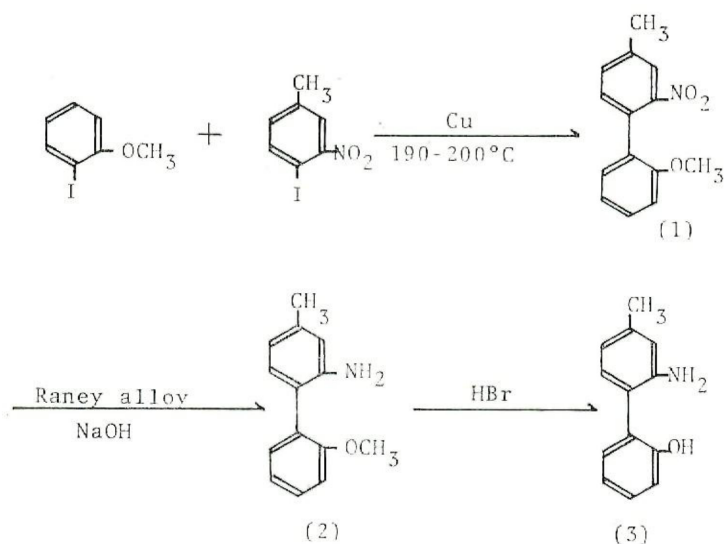


Fig. 1 The synthetic scheme of Hambp(3)

The UV, IR, NMR and mass spectral properties of Hambp(3) showed that the compound had a normal aromatic aminophenol structure(3). In the IR spectra of Hambp(3) and its complexes shown in Table 1, the band due to the O-H stretching vibration of the phenolic hydroxyl group was found at 3500 cm^{-1} . The bands for O-H stretching vibration for the complexes of Com-Cu₅ and Com-Cu₂ were observed at 3430 and 3530 cm^{-1} , respectively. The band due to the C-O vibration of the phenolic hydroxyl group was found at 1230 cm^{-1} . In the spectra of the copper(II) complexes, however, the band at 1230 cm^{-1} was shifted to a lower-frequency region by $15\sim 20\text{ cm}^{-1}$. A new band around 1550 cm^{-1} indicated that the phenolic oxygen is involved with the coordination. The N-H stretching vibrations were shifted to a lower-frequency region by $20\sim 100\text{ cm}^{-1}$ by the complex formation. These facts indicate that both the phenolic oxygen and amino nitrogen of Hambp(3) participate in the coordination, and that Hambp(3) acts as a bidentate chelating agent to form copper(II) complexes with seven-membered chelate rings. By examining the UV spectra of these complexes in methanol shown in Fig. 2, d-d transition bands are found in the region of $14\sim 16\times 10^3\text{ cm}^{-1}$. The Com-Cu complex had a magnetic moment of 1.84 B. M. at room temperature.

Table 1. IR absorption bands of Hambp and its complexes. (cm^{-1})

	νOH	νNH_2	New bands	$\delta\text{C-O}$	
Hambp	3500	3370 3290	— —	1230	KBr disk
Com-Cu	—	3325 3205	1540 —	1250	KBr disk
Com-Cu ₅	3430	3290 3190	1545 —	1245	KBr disk
Com-Cu ₂	3530	3350 3225	1547 1700	1250	KBr disk
		(3300 3200)	CCl ₄ Mull		

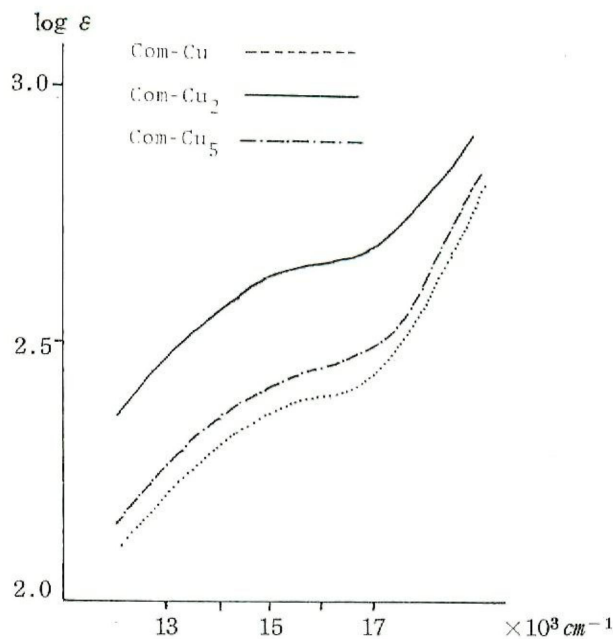


Fig. 2 UV spectra of Complexes (36.8mg/25mlMeoH)

Com-Cu₂ Complex: When Com-Cu complex was refluxed in ethyl acetate, Com-Cu₂ complex was obtained. In the infrared spectrum of Com-Cu₂, the C=O stretching vibration of ethyl acetate was observed at 1700 cm⁻¹, and the band at 1380 cm⁻¹ due to the methyl group was more enhanced in intensity than that of Com-Cu. This complex showed 12.9% of drying loss. These facts indicate that one mole of each ethyl acetate and water were added to the complex, although they were not coordinated. The elemental analysis of this complex suggested the binuclear composition. The effective magnetic moment of Com-Cu₂ is 1.66 B.M. at room temperature.

Com-Cu₅ Complex: When Com-Cu complex was refluxed in benzene, Com-Cu₅ was obtained. The elemental analysis of this complex suggested the pentanuclear composition. The effective magnetic moment of Com-Cu₅ is 1.38 B. M. at room temperature.

Experimental

Syntheses: 2-Methoxy-2'-nitro-4'-methylbiphenyl(I):

2-Iodoanisole²⁾ (200g), 3-nitro-4-iodotoluene (100g) and copper powder³⁾ (200g) were mixed together and heated to about 190~200°C in an oil bath with stirring for two hours. The reaction mixture was then cooled and extracted with benzene. The benzene solution was distilled, and the fraction of 177~190°C at 5 mmHg was collected and treated with cold methanol, from which most of 2,2'-dimethoxybiphenyl was crystallized

out. The filtrate gave, after concentration and addition of water, crude 2-methoxy-2'-nitro-4'-methylbiphenyl(2), which was subsequently purified by recrystallization from aqueous methanol. Pale yellow needles; mp 106.3~106.8°C; 11.6 g, 19.3%. NMR: δ (ppm) 2.38 (singlet, CH_3), 3.61 (singlet, 3H, OCH_3), 7.10 (multiplet, 7H, aromatic protons). Mass spectrum: m/e 244 ($\text{M}+1$, 15.2% of M^+), 212, 198, 181, 152, 141, 129, 115 and 76. Found: C, 68.99; H, 5.36; N, 5.78%. Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_3$: C, 69.12; H, 5.39; N, 5.76%.

2-Amino-4-methyl-2'-methoxybiphenyl(2):

2-Methoxy-2'-nitro-4'-methylbiphenyl(I) (7.5 g) was dissolved in hot methanol (100ml), to which aqueous sodium hydroxide solution (20%, 100 ml) was added with warming. Raney alloy (powder, 10 g) was then added, little by little, to the above solution under stirring. After the addition had been completed, the mixture was stirred for more than 20 min. and the excess metal was filtered off, while the solution was still hot. The reaction mixture was then cooled and extracted with benzene. The benzene solution was distilled and the residue was recrystallized from aqueous methanol. Colorless needles, mp 55.5~56.7°C, 5.1 g, 77.6%. NMR: δ (ppm) 2.31 (singlet, 3H, CH_3), 3.76 (singlet, 3H, OCH_3), 6.80 (multiplet, 7H, aromatic protons). Mass spectrum: m/e 214 ($\text{M}+1$, 15% of M^+), 213 (M^+), 194, 182, 167, 154, 115 and 77. Found: C, 78.58; H, 7.08; N, 6.61%. Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}$: C, 78.84; H, 7.09; N, 6.57%.

2'-Amino-4'-methylbiphenyl-2-ol(Hampb) (3): A mixture of 2-amino-4-methyl-2'-methoxybiphenyl(2) (4.5 g) and hydrobromic acid (47%, 40 ml) was gently refluxed for one hour. The mixture was then cooled and poured into water. The aqueous solution was neutralized with a dilute aqueous ammonium hydroxide solution, and the precipitate was collected by filtration. The precipitate was recrystallized from aqueous methanol. Colorless needles, mp 81.5~82.0°C, 3.0 g, 71.4%. NMR: δ (ppm) 2.30 (singlet, 3H, CH_3), 4.45 (singlet, 3H, NH_2 and OH), 7.00 (multiplet, 7H, aromatic protons). Mass spectrum: m/e 200 ($\text{M}+1$, 12% of M^+), 199 (M^+), 182, 167, 154, 115 and 77. Found: C, 78.13; H, 6.59; N, 7.08%. Calcd for $\text{C}_{13}\text{H}_{14}\text{NO}$: C, 78.46; H, 6.59; N, 7.03%.

$[\text{Cu}(\text{ampb})_2(\text{Hampb})] \cdot 1/4\text{H}_2\text{O}$: Copper acetate (50 mg) was dissolved in water (10 ml), to which an aqueous ammonium hydroxide solution (28%, 1 ml) was added and kept at 50~60°C. A solution of Hampb (112.5 mg) in small amount of ethanol was added to the above solution. The precipitate was then filtered off and washed with water and then with a small amount of ethanol. Dark brown needles, mp 199~200°C, 111.5 mg, 90.0%. Found: C, 70.70; H, 5.85; N, 6.18; Cu, 8.61%. Calcd for $\text{C}_{39}\text{H}_{37}\text{N}_3\text{O}_3\text{Cu} \cdot 1/4\text{H}_2\text{O}$: C, 70.57; H, 5.69; N, 6.33; Cu, 9.56%.

$\text{Cu}_5(\text{ampb})_8(\text{OH})_2$: Com-Cu complex was warmed in benzene at 60~70°C for about 40 min. The precipitate was filtered off, washed with benzene, and dried

for a short time. Dark brown needles, mp 165~170°C (decomp). Found: C, 64.41; H, 4.97; N, 5.48; Cu, 16.43%. Calcd for $\text{Cu}_5(\text{ambp})_8(\text{OH})_2$: C, 64.46; H, 5.09; N, 5.78; Cu, 16.41%.

$\text{Cu}_2(\text{ambp})_3(\text{OH}) \cdot \text{CH}_3\text{COOC}_2\text{H}_5 \cdot \text{H}_2\text{O}$: This complex was prepared from Com-Cu complex by boiling it in ethyl acetate. The precipitate was filtered off, washed with ethyl acetate, and air-dried for a short time. Brown needles, mp 224~225°C. The complex was insoluble in water but slightly soluble in ethanol and acetone. Found: C, 60.29; H, 5.55; N, 4.54; Cu, 15.67%. Drying loss (110°C, 3 hrs.) = 12.9%. Calcd for $\text{Cu}_2(\text{ambp})_3(\text{OH}) \cdot \text{CH}_3\text{COOC}_2\text{H}_5 \cdot \text{H}_2\text{O}$: C, 59.90; H, 5.50; N, 4.88; Cu, 14.76%. $\text{CH}_3\text{COOC}_2\text{H}_5$ and H_2O = 12.6%.

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