# Syntheses and Properties of 2′-Aminobiphenyl-2-ol and Its Copper(II) Complexes

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A new bidentate ligand, 2′-aminobiphenyl-2-ol(Habp), 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: $Cu(abp)_2$, $Cu(abp)_2 \cdot H_2O$, $Cu(abp)_2 \cdot C_6H_6$, $Cu(abp)_2 \cdot CH_3COOC_2H_5$, and $Cu_5(abp)_8(OH)_2 \cdot 3H_2O$.

Only a few examples of mononuclear metal complexes[1] with seven-membered chelate rings derived from bidentate ligands have been reported. It is generally accepted that the complexes with chelate rings of more than six members are often unstable and tend to give polynuclear complexes. 2-Aminophenol is a well-known complexing agent, and so the author was tempted to examine the seven-membered analogue of bis-(2-aminophenolato) copper(II) from the above point of view.

The present report will describe the syntheses and characterizations of the new ligand, 2′-aminobiphenyl-2-ol (abbreviated as Habp), and its copper(II) complexes; these studies led to the conclusion that the ligand gives mono- or polynuclear complexes, depending on the reaction conditions.

The aminophenol (**3**) was synthesized according to the scheme shown in Fig. 1. The dissolving-metal reduction of 2-methoxy-2′-nitrobiphenyl (**1**) with Raney alloy led to 2-amino-2′-methoxybiphenyl (**2**), which was then demethylated with boiling hydrobromic acid giving Habp (3) in a fair yield.

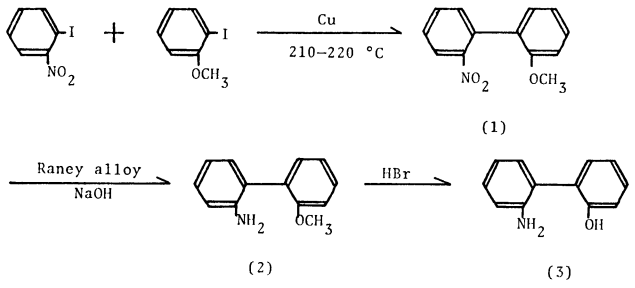


Fig. 1. The synthetic scheme of Habp.

When the ligand was treated with copper(II) ions in an ammoniacal aqueous ethanolic solution, the complex of the composition, $Cu(abp)_2 \cdot H_2O$, was obtained in the form of brown needles. The complex gave $Cu(abp)_2 \cdot C_6H_6$ or $Cu(abp)_2$ when heated with benzene, and $Cu(abp)_2 \cdot CH_3COOC_2H_5$ when heated with ethyl acetate. As will be discussed below, an examination of the IR, UV, and magnetic susceptibilities showed that the complexes had mononuclear structures. On the other hand, however, when the ligand was reacted with copper acetate in an aqueous ethanolic solution, a copper complex of a different composition was obtained; it was confirmed to have a polynuclear, probably a pentanuclear structure, by a study of its elementary analytical, spectral, and magnetic properties.

## Experimental

*Syntheses.* *2-Methoxy-2′-nitrobiphenyl (1)*:[2] *o*-Iodonitrobenzene[3] (200 g), *o*-iodoanisole[4] (200 g), and copper powder[5] (200 g) were mixed and heated at 210—220 °C in an oil bath under stirring for one and a half hour. The reaction mixture was then cooled and extracted with benzene. The benzene solution was distilled, and the fraction between 160—190 °C, 7 mmHg was treated with cold methanol, from which most of the 2,2′-dimethoxybiphenyl crystallized out. The filtrate gave, after concentration and the addition of water, crude methoxynitrobiphenyl (**1**), which was subsequently purified by recrystallization from aqueous methanol. Pale yellow needles; mp 78 °C; 61.2 g, (31.2%). Found: C, 68.09; H, 4.78; N, 6.32%. Calcd for $C_{13}H_{11}O_3N$: C, 68.11; H, 4.84; N, 6.11%.

*2-Amino-2′-methoxybiphenyl (2)*: 2-Methoxy-2′-nitrobiphenyl (**1**) (20 g) was dissolved in a mixture of ethanol (95%, 100 ml) and an aqueous sodium hydroxide solution (20%, 100 ml) by warming. Raney alloy (powder, 20 g) was added, little by little, to the above solution under stirring. After the addition had been completed, the mixture was stirred for a further 20 min and filtered while hot. The subsequent concentration of the filtrate separated an oil which solidified on cooling. It was then distilled under diminished pressure, and the fraction which distilled between 157—159 °C/5.5 mmHg was recrystallized from aqueous methanol. Colorless needles; mp 78—79 °C; 13.6 g (78%). (The yield was 56% when iron powder and hydrochloric acid were used for the reduction.) Found: C, 77.93; H, 6.57; N, 7.83%. Calcd for $C_{13}H_{13}NO$: C, 78.39; H, 6.53; N, 8.04%.

*2′-Aminobiphenyl-2-ol (Habp) (3)*: A mixture of 2-amino-2-methoxybiphenyl (**2**) (10 g) and hydrobromic acid (48%, 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 and washed with water. The precipitate was then further purified by sublimation under reduced pressure. Colorless needles; mp 91—92 °C; 6.5 g, (70%). IR, Table 1. UV; $\lambda_{max}$, 263 nm (no appreciable absorption in the visible region). NMR; $\delta$ (ppm) 4.29 (singlet, 3H, $N\underline{H}_2$ and $O\underline{H}$), 7.12 (multiplet, 8H, aromatic protons). Mass Spectrum; *m/e* 186 ($M+1$, 14% of $M^+$), 185 ($M^+$), 168, 156, 154, 139, 129, 89, 77 and 65. Found: C, 77.84; H, 6.02; N, 7.63%. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.98; N, 7.56%.

*$Cu(abp)_2 \cdot H_2O$*: Copper acetate (33 mg) was dissolved in water (3 ml) containing an aqueous ammonium hydroxide solution (28%, 0.5 ml) and kept at 50—60 °C. A solution

of Habp (62 mg) in ethanol (1 ml) was then added to the above solution. The precipitate was filtered and washed with water and then with a small amount of ethanol. Reddish orange needles; 65 mg, (91%). Found: C, 64.29; H, 4.82; N, 6.22; Cu, 13.94%. Calcd for $C_{24}H_{20}N_2O_2Cu \cdot H_2O$: C, 64.03; H, 4.93; N, 6.22; Cu, 14.13%.

*Cu(abp)$_2$·C$_6$H$_6$*: Cu(abp)$_2$·H$_2$O was warmed in benzene at 60 °C for 40 min. The precipitate was filtered, washed with benzene, and air-dried for a short time. Brown needles. Found: C, 70.08; H, 5.10; N, 5.52; Cu, 12.42%. Drying loss (80 °C, 5 mmHg, 8 hr), 14.9%. Calcd for $C_{24}H_{20}N_2O_2Cu \cdot C_6H_6$: C, 70.05; H, 5.10; N, 5.62; Cu, 12.67; $C_6H_6$, 15.30%.

*Cu(abp)$_2$*; When Cu(abp)$_2$·H$_2$O was boiled with benzene for one hour, an anhydrous complex was obtained in the form of dark brown needles. Found: C, 66.73; H, 4.70; N, 6.15; Cu, 14.53%. Calcd for $C_{24}H_{20}N_2O_2Cu$: C, 66.74; H, 4.67; N, 6.49; Cu, 14.71%.

*Cu(abp)$_2$·CH$_3$COOC$_2$H$_5$*: This complex was prepared from Cu(abp)$_2$·H$_2$O by boiling it in ethyl acetate. Glistening brown needles. Found: C, 64.08; H, 5.48; N, 5.35; Cu, 14.50%. Calcd for $C_{24}H_{20}N_2O_2Cu \cdot CH_3COOC_2H_5$: C, 64.66; H, 5.44; N, 5.38; Cu, 14.70%.

*Cu$_5$(abp)$_8$(OH)$_2$·3H$_2$O*; To a solution of copper acetate (82 mg) in water (4 ml), we added a solution of Habp (122 mg) in ethanol (3 ml), after which the mixture was kept at 50—60 °C. The precipitate was then filtered and washed with water. Brownish green needles; 131 mg (85%). The complex was insoluble in water and slightly soluble in organic solvents. Found: C, 61.36; H, 4.65; N, 5.67; Cu, 16.97%. Calcd for $Cu_5(abp)_8(OH)_2 \cdot 3H_2O$: C, 61.34; H, 4.72; N, 5.69; Cu, 16.90%. Calcd for $Cu_3(abp)_5(OH) \cdot 3H_2O$: C, 60.87; H, 4.90; N, 5.91; Cu, 16.10%.

*Measurements*; The infrared spectra were taken by means of a Hitachi EPI-S2 spectrophotometer in the 650—4000 cm$^{-1}$ region, mostly on a KBr disk. The electronic spectra in solutions and on solid samples were measured with a Hitachi EPI-3T recording spectrophotometer. The NMR spectrum was taken with a Hitachi R-24 spectrometer (60 MHz, $CDCl_3$, reference TMS), and the mass spectrum, with a Hitachi RMU-6L mass spectrometer.

The magnetic susceptibilities of the complexes were measured by the Faraday method. The temperature variation in the magnetic susceptibility was measured by the Gouy method in the range from the temperature of liquid nitrogen to room temperature. The effective magnetic moments, $\mu_{eff}$, were determined by means of this equation;

$$\mu_{eff} = 2.83\sqrt{(\chi_A - N_\alpha)T}$$

where $\chi_A$ is the atomic susceptibility corrected by the use of Pascal's constants[6] for diamagnetism, and $N_\alpha$, the temperature-independent paramagnetism of the copper(II) ion ($60 \times 10^{-6}$ cgs, emu).[7]

## Results and Discussion

An examination of the UV, IR, NMR, and mass spectra of Habp did not reveal any particular deviation from the expected properties as a normal aromatic aminophenol with Structure (3).

In the IR spectrum of Habp, the band due to the O–H stretching vibration of the phenolic hydroxyl group was found at 3400 cm$^{-1}$. The bands in the 2500—2700 cm$^{-1}$ region cannot be assigned definitely at present. These bands, however, could not be observed in the spectra of the copper(II) complexes. Instead a new band was observed around 1550 cm$^{-1}$. It is known that such a new band appears when the phenolic oxygen is involved with the coordination. The N–H stretching vibrations were shifted to a lower-frequency region by 65—105 cm$^{-1}$ by the complex formation. These facts indicate that both the phenolic oxygen and amino nitrogen of Habp participate in the coordination, and that Habp acts as a bidentate chelating agent to form copper(II) complexes with seven-membered chelate rings. The band at 685 cm$^{-1}$ for Cu(abp)$_2$·C$_6$H$_6$ and the bands at 1705 and 1380 cm$^{-1}$ for Cu(abp)$_2$·CH$_3$COOC$_2$H$_5$ may be attributed to the benzene and ethyl acetate molecules respectively.

The water molecule in Cu(abp)$_2$·H$_2$O is not considered to be coordinated to the copper(II) ion, since it is easily removable at a relatively low temperature. The reflectance spectrum of this complex (given in Fig. 2) shows the d-d band at $13.9 \times 10^3$ cm$^{-1}$; it is

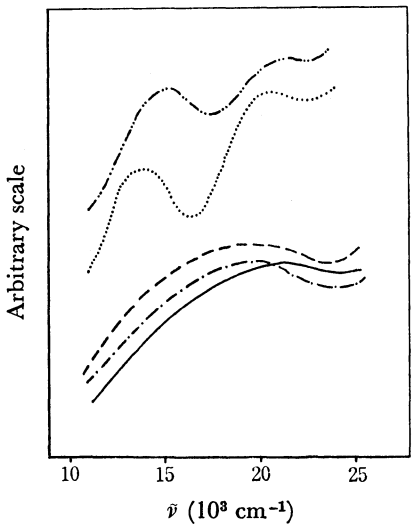


Fig. 2. The reflectance spectra of (abp)–Cu(II) complexes.

-·-·- $Cu_5(abp)_8(OH)_2 \cdot 3H_2O$ ····· $Cu(abp)_2 \cdot H_2O$
---- $Cu(abp)_2 \cdot C_6H_6$ —— $Cu(abp)_2$
-·-· $Cu(abp)_2 \cdot CH_3COOC_2H_5$

Table 1. IR absorption bands of Habp and its complexes

| | $\nu$OH | $\nu$NH$_{as.}$ | $\nu$NH$_s$. | | | | New bands in the complexes ($\nu$C–O) | | | $\delta$C–O | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Habp | 3400 | 3360 | 3300 | 2750, | 2670, | 2570 | — | — | — | 1218 | KBr disk |
| Habp | 3550 | 3450 | 3350 | — | — | — | — | — | — | 1230 | $CCl_4$ mull |
| Cu(abp)$_2$ | — | 3255 | 3175 | — | — | — | 1547 | | | 1217 | KBr disk |
| Cu(abp)$_2$·C$_6$H$_6$ | — | 3300 | 3200 | — | — | — | 1550, | 685 | | 1215 | KBr disk |
| Cu(abp)$_2$·CH$_3$COOC$_2$H$_5$ | — | 3275 | 3195 | — | — | — | 1550, | 1705, | 1380 | 1218 | KBr disk |
| Cu$_5$(abp)$_8$(OH)$_2$·3H$_2$O | — | 3300 | 3225 | — | — | — | 1555 | | | 1235 | KBr disk |

Table 2. The effective magnetic moments (B.M.) over a temperature range of $Cu_5(abp)_8(OH)_2 \cdot 3H_2O$

| $T$(K) | 76.4 | 96.0 | 119.1 | 142.1 | 170.3 | 200.0 | 219.0 | 241.5 | 274.7 | 295.7 |
|---|---|---|---|---|---|---|---|---|---|---|
| $\chi_A \cdot 10^6$ | 2737 | 2190 | 1824 | 1557 | 1351 | 1206 | 1122 | 1065 | 967 | 925 |
| $\mu_{eff}$ | 1.27 | 1.28 | 1.29 | 1.30 | 1.33 | 1.35 | 1.36 | 1.40 | 1.41 | 1.43 |

significantly lower in energy than that of bis-(2-aminophenolato) copper(II) (*ca.* $16 \times 10^3$ cm$^{-1}$). This indicates that the configuration of $Cu(abp)_2 \cdot H_2O$ is considerably distorted from the square-planar structure. Since it is well established that the red shift in the d-d band takes place when the geometry around the copper(II) ion is distorted from planarity,[8] the pseudo-tetrahedral configuration of this complex can also be expected in the examination of the molecular model.

The benzene molecule in $Cu(abp)_2 \cdot C_6H_6$ and the ethyl acetate molecule in $Cu(abp)_2 \cdot CH_3COOC_2H_5$ are also considered to be kept between crystal lattices, since the coordination of benzene to copper(II) ion seems unlikely and since it is clear from the IR spectrum that the ethyl acetate molecule is not coordinated to the copper(II) ion. In fact, the reflectance spectra of $Cu(abp)_2$, $Cu(abp)_2 \cdot C_6H_6$, and $Cu(abp)_2 \cdot CH_3COOC_2H_5$ (given in Fig. 2) are very similar to each other, demonstrating that they have nearly the same molecular structure. Although the d-d bands of these complexes are not well-defined, it is assumed, considering the steric requirement of the ligand, that the complexes have pseudo-tetrahedral structures. The absorption band around the $20 \times 10^3$ cm$^{-1}$ region which is common in all these complexes is thought to be a kind of charge-transfer band between the ligand and the copper(II) ion. The effective magnetic moments of $Cu(abp)_2 \cdot H_2O$, $Cu(abp)_2$, $Cu(abp)_2 \cdot C_6H_6$, and $Cu(abp)_2 \cdot CH_3COOC_2H_5$ at room temperature are 1.77, 1.78, 1.88, and 1.85 B.M respectively.

The d-d band of the polynuclear complex appears at $15.1 \times 10^3$ cm$^{-1}$. The effective magnetic moment at room temperature was 1.43 B.M., significantly lower than that of the spin-only value (1.73 B.M.). As can be seen in Table 2, the effective magnetic moment of the complex decreases with a decrease in the temperature and approaches 1.27 B.M. near the temperature of liquid nitrogen. This fact implies that this is a polynuclear copper(II) complex composed of an odd number of copper(II) ions, in which an antiferromagnetic spin-exchange interaction operates (spin-doublet ground state). Therefore, the magnetic property of the polynuclear complex is consistent with the composition of the complex, $Cu_5(abp)_3(OH)_2 \cdot 3H_2O$, as determined by elementary analysis.

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