Copper (2) Complex with Seven- Membered Chelate Rings - Syntheses and properties of 1,1'-bi -2- naphthol and its copper (2) complex -

Copper(II) Complex with Seven-Membered Chelate Rings.

—— Syntheses and properties of 1,1'-bi-2-naphthol and its copper(II) complex ——

by

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Only a few coordination compounds with seven-membered chelate rings with a bidentate ligands have been known up to date. The reason may have been due to the instability of such a compounds known so for, are tetramethylenediamine, succinate and biphenyl complexes[1].

It has been studied that the biphenyl derivative compound is a bidentate ligand which form a stable copper(II) complex with seven-membered chelate rings.

In this study, 1,1'-bi-2-naphthol (abbreviated as H_2bnp) and its copper(II) complex, $[Cu(Hbnp)_2\cdot(NH_3)_2]_n$, were synthesized. The compound of H_2bnp was obtained by the oxydation of β-naphthol with ferric(III) chloride in accordance with the process given in Fig. 1. From aqueous ammoniac solution of copper acetate and associated compound above, $[Cu(Hbnp)_2\cdot(NH_3)_2]_n$ was obtained successively.

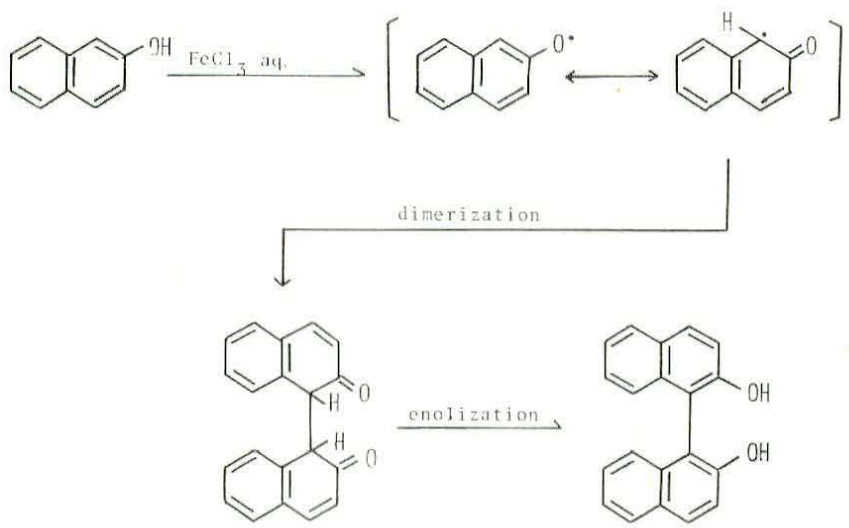

Fig. 1. Synthetic scheme of H_2bnp

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Result and Discussion

In the IR spectrum of the ligand H_2bnp shown in Fig. 2, the band due to the C-O stretching vibration of the phenolic hydroxyl group was found at 1380 cm^{-1}. This band, however, could not be observed in the spectrum of the copper (II) complex shown in Fig. 3. A new band, instead, at 1545 cm^{-1} in which H.Okawa and S.Kida[2] pointed out that the band is resulted from a skeletal vibration of the aromatic ring, was observed. The broad bands around 3400 and 2500 cm^{-1} may probably be due to the uncoordinated ammonium ion groups as the elementary analysis of this complex exhibit the existence of nitrogen.

The UV spectrum of the complex in chloroform shown in Fig. 4, displays a d-d band of the complex appears at $17.0 \times 10^3 cm^{-1}$. The magnetic morment at the room temperature (18.5℃) is 1.04 B. M., that is markedly smaller than the "spin-only value" of 1.73 B. M.. This facts implies that this is a polynuclear copper (II) complex suggesting a strongly antiferromagnetic spin-exchenge interaction between the copper (II) ions. In facts, the elementary analysis of the complex suggest a possible molecular formula of $Cu(Hbnp)_2 \cdot (NH_3)_2$. From these facts, it can be presumed that the complex is polymerized consisting with the composition of the complex, $[Cu(Hbnp)_2 \cdot (NH_3)_2]_n$.

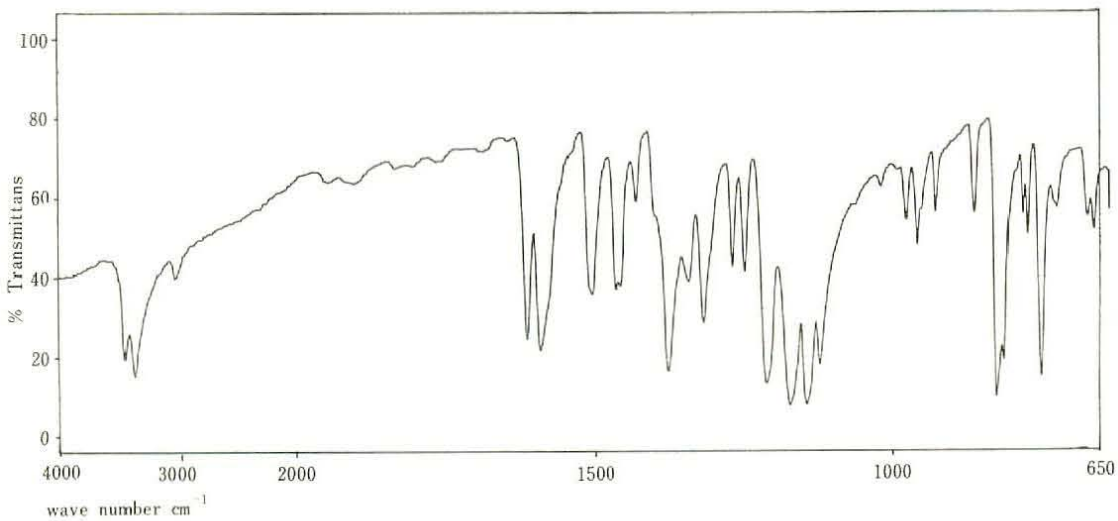

Fig. 2 IR Spectrum of H_2bnp (KBr disk)

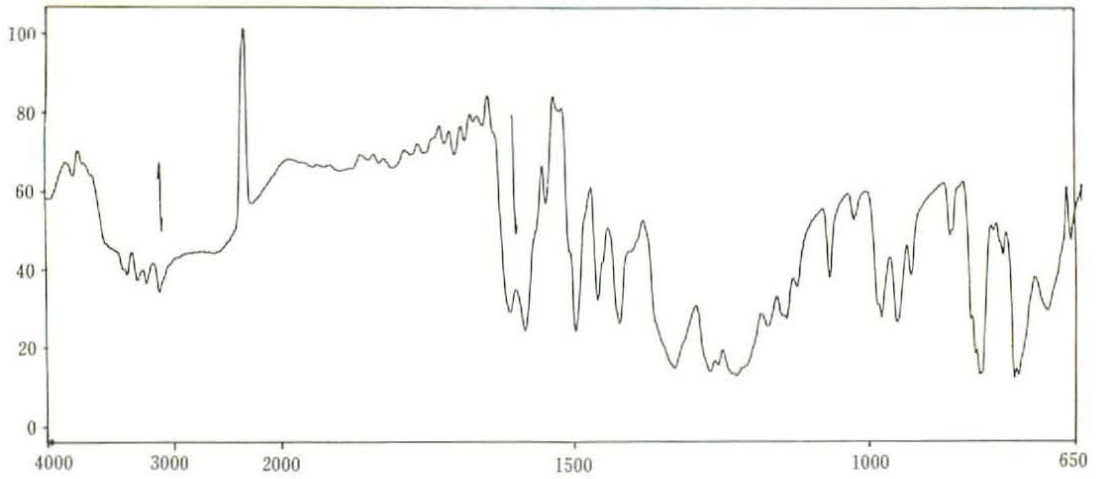

Fig. 3 IR Spectrum of Hbnp-Cu(II) Complex. (KBr disk)

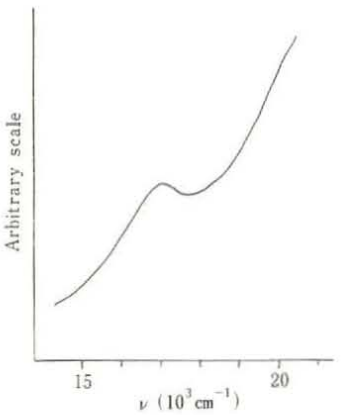

Fig. 4 UV Spectrum of Hbnp-Cu(II) Complex.

Measurments

The infrared spectra were obtained with Hitachi EPI-S-2 spectrophotometer in the region from 4000 to 650 cm^{-1}, using the KBr disk. The mass spectra were obtained by using Hitachi RMU-6L spectrometer, and UV spectra, with Hitachi EP S-3-T spectrophotometer.

The magnetic susceptibilities of the complex was measured by the Faraday method. The effective magnetic morments μ_{eff}, were evaluated by means of the following equation: $\mu_{eff} = 2.83\sqrt{(\chi_A - N_a)\,T}$

where χ_A is the atomic susceptibility corrected for diamagnetism by the use of Pascal's constants and $N\alpha$, the temperature-independent paramagnetism of the copper(II) ion (60×10^{-6} *cgs, emu*).[3]

Experimental

1) Synthesis of 1,1'-bi-2-naphthol (H_2bnp)

A mixture of β-naphol (20 *g*) and aqueous ferric(III) chloride solution (10%, 500 *ml*) was gently refluxed for five hours. The mixture was then cooled and the precipitate appeared was collected by filtlation. It was then washed with water, and was recrystallized from aqueous methanol. Colorless needles were obtained with mp 216.5-217.2°C by 90% (18 *g*) yield.

From the studies of IR and mass spectra (M^+, m/e 286; M+1, 22% of M^+), it was found that the compound mention above has already been recognized as known substance.

2) Synthesis of $[Cu(Hbnp)_2 \cdot (NH_3)_2]_n$.

Copper acetate (350 *mg*) was dissolved in water (10 *ml*) containing an aqueous ammonium hydroxide solution (28%, 3 *ml*) and kept at 50-60°C. A solution of H_2bnp (500 *mg*) in ethanol (2 *ml*) was added to the above solution. The precipitate produced was then filtered off and washed with water and then with a small amount of ethanol. Brown needles were obtained with mp 223-224.5°C by 97.4% (570 *mg*) yield. The obtained complex was insoluble in water and in any organic solvents tested.
Found: C, 71.59; H, 4.76; N, 3.83; Cu, 9.36%. Calcd. for
$C_{40}H_{32}H_2O_4Cu$: C, 71.89; H, 4.83; N, 4.16; Cu, 9.51%.

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