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Copper(II) Complex of 2,2′-Bi-8-quinolinol

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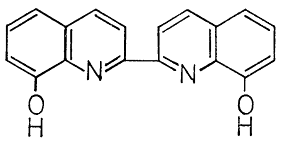
A copper(II) complex of 2,2′-bi-8-quinolinol was prepared. The structure has been determined by means of infrared and electronic spectra, magnetic susceptibility under temperature variation, and molecular weight measurement. It was found to be a binuclear chelate having a tetrahedral arrangement around each copper ion.

8-Quinolinol functions as a bidentate ligand and forms stable chelates with a variety of metal ions as well as copper(II). The high stability of the complexes is mainly attributable to the fixed planar ligand structure containing a phenolic oxygen and a heteroaromatic nitrogen atom. On the other hand, 2,2′-biquinoline is known as a specific ligand for copper(I), and this property is due to the steric fitness of the ligand structure together with the stabilization of low oxidation state by the α-diimine coordination. It is of interest to prepare the compound in which these two functions are combined in one molecule. We thus have synthesized 2,2′-bi-8-quinolinol (**1**) and examined its complex formation with transition metal ions, and well defined crystals have been obtained with copper(II). In this paper we will deal with the synthesis of the ligand and the copper complex, and will discuss its structure by means of electronic and infrared spectroscopy and of magnetic measurement at various temperature.

Results and Discussion

2,2′-Bi-8-quinolinol (**1**) was prepared in poor yield by the dimerization of 2-bromo-8-tosyloxyquinoline with palladium-calcium carbonate catalyst in the presence of hydrazine according to the method developed by Nakano.[1] The tosyl group was hydrolyzed simultaneously during the dimerization reaction.



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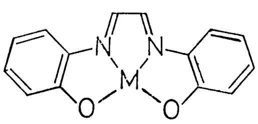

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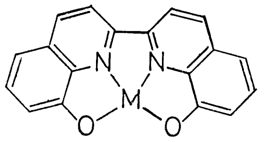

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1 is considered as a heterocyclic analogue of *N,N′*-bis(*o*-hydroxyphenyl)-1,2-ethanediimine[2] in which the azomethine linkages are incorporated into heteroaromatic rings. *N,N′*-Bis(*o*-hydroxyphenyl)-1,2-ethanediimine functions as a planar quadridentate ligand and forms deep blue chelates **2** with copper(II) and other transition metal ions. Provided that **1** forms a copper chelate in the similar manner as shown in **3**, a molecular model reveals that the Cu–N and Cu–O distances are about 0.2 nm and 0.3 nm respectively, unless the quinoline moieties bend towards the central metal ion. The Cu–O distance will be too long to achieve stable coordination as compared with those in bis(8-quinolinolato)copper(II) in which the Cu–N and the Cu–O distances are 0.19 nm and 0.21 nm respectively.[3]

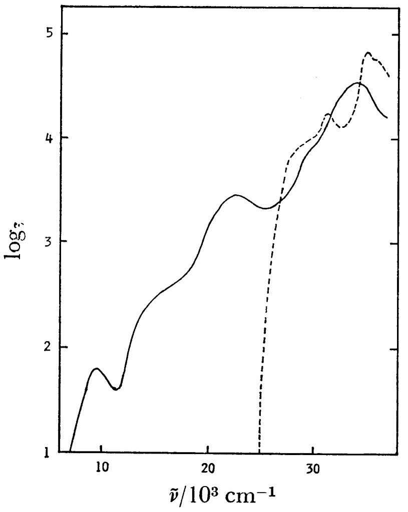

Fig. 1. Electronic spectrum of the free ligand (**1**) (- - -), and the Cu(II) complex (——).

The copper(II) complex is deep brown fine crystals and the elemental analysis agrees with the metal-ligand ratio of 1:1. However, the molecular weight determined in chloroform was 708 and it is very close to the calculated value as a dimer (700).

The infrared spectral pattern in KBr resembles that of bis(8-quinolinolato)copper(II) in many respects, especially showing a sharp absorption at 1105 $\mathrm{cm^{-1}}$ which is characteristic for a C–O stretching vibration in metal 8-quinolinolates.[4] No absorption is observed for the OH stretching which appears as a sharp band at 3350 $\mathrm{cm^{-1}}$ in the free ligand. The electronic spectrum in chloroform exhibits an absorption maximum at 34000 $\mathrm{cm^{-1}}$(ε=35500), 22200(ε=2900), 14300(ε=300), and 9300(ε=90) as seen in Fig. 1. The spectral pattern is quite different from those usually associated with bivalent copper in square-planar arrangements. Similar spectrum has been observed for bis(2,2′-biquinoline)copper(II) perchlorate, which exhibited d-d transition at 19230 $\mathrm{cm^{-1}}$(ε=950), 13300(ε=170), and 9300

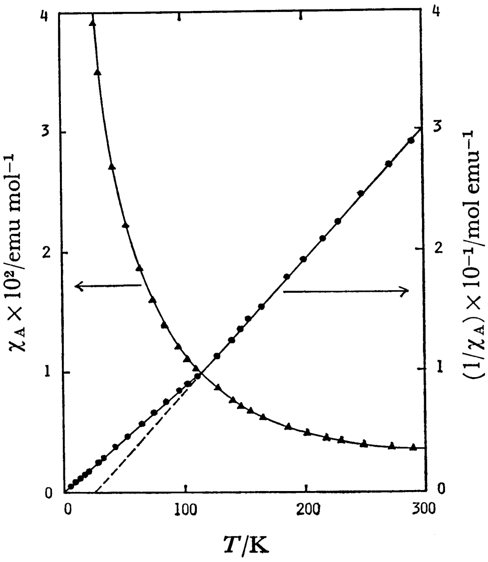

Fig. 2. Temperature variation of molar and inverse magnetic susceptibilities of the complex. The diamagnetic correction was -3.11×10^{-4}.

(ε=90) in nitrobenzene.[5] {2,2′-[1,1′-Biphenyl-2,2′-diyldinitrilomethylidyne]bisphenolato}copper(II) also showed absorptions at 20800 cm^{-1}(ε=790), 15200(ε=340), and 11500(ε=50).[6] These complexes have been assumed to have a pseudo tetrahedral structure and the latter was confirmed by X-ray crystallography.[7]

The variation of the magnetic susceptibility under temperature change is shown in Fig. 2. The susceptibility obeys Curie-Weiss' law in the temperature range 118—290.8 K with a value of θ=20.5 K, while it obeys Curie's law between 5.7—118 K. This temperature dependence of χ_A suggests that the copper(II) ions are not magnetically isolated but under some magnetic interaction. Provided a binuclear structure exists, the χ_A is given as the Bleaney-Bowers' equation,[8]

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp\left(-2J/kT\right)\right]^{-1} + N_\alpha,$$

where N is the Avogadro constant, β the Bohr magneton, k the Boltzman constant, T the temperature, J the exchange integral, and the N_α the temperature-independent paramagnetism. The experimental $|J|$/K value which fits this equation best is 200 K below 118 K, and 120 K at higher temperature, where N_α is 1×10^{-4} emu/mol. The μ_{eff} values for one copper ion are 2.02 BM(290.8 K), 2.15(118.3 K), and 2.29 (5.7 K). The room temperature value is slightly lower than that (2.2 BM) predicted for copper(II) in a tetrahedral environment.[9] However, distortion can appreciably lower it, if low symmetry ligand fields produced are large compared to the spin-orbit coupling, and similar values (1.9—2.0 BM) have been reported for bis(2,2′-biquinoline)copper(II).[5]

Judging from the dimeric molecular weight, the electronic spectrum, and the magnetic evidence, the copper(II) complex prepared is binuclear and the ligands are tetrahedrally arranged around the copper ions. A molecular model can be sketched as shown in Fig. 3. Here one quinolinol plane is nearly perpendicular to the other in one biquinolinol molecule, and each quinolinol moiety is individually coordinated to each of the two copper ions. The data obtained so far support the proposed structure, though the definite conclusion must wait for X-ray crystallography.

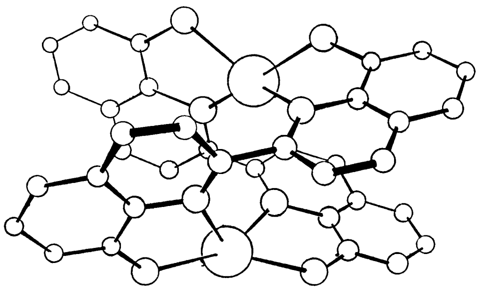

Fig. 3. Probable structure of the complex.

Experimental

2-Bromo-8-tosyloxyquinoline. A mixture of 8-tosyloxy-2(1*H*)-quinolinone (22.5 g) and phosphoryl bromide (50 g) in 40 cm^3 chloroform was refluxed with stirring in an oil bath at 110 °C for 4 h. The reaction mixture was poured into crashed ice and the water layer was neutralized with 5% aqueous sodium hydrogencarbonate. The chloroform layer was collected and the aqueous layer was extracted twice with 150 cm^3 of chloroform. The combined extracts were dried over anhydrous sodium sulfate and the solvent was removed by distillation. The crude residual product was recrystallized from ethanol and 24 g of the compound were obtained as colorless crystals, mp 133 °C, yield 80%.

Found: C, 50.55; H, 3.19; N, 3.70%. Calcd for $C_{16}H_{12}BrNO_3S$: C, 50.80; H, 3.18; N, 3.70%.

2,2′-Bi-8-quinolinol. 2-Bromo-8-tosyloxyquinoline (5 g) was dissolved in 200 cm^3 of methanol containing 5% potassium hydroxide and 3 g of 2% palladium on calcium carbonate was added. The mixture was heated at 50 °C and to this was added dropwise with stirring 6 cm^3 of hydrazine hydrate in 50 cm^3 methanol. The addition took 4 h and 3 g of the catalyst was newly added after 2 h during the reaction. After the addition of hydrazine, the reaction mixture was further heated at 80 °C for 1 h. The catalyst was filtered off and the mixture was treated with 500 cm^3 of hot 5% potassium hydroxide–methanol solution. The filtrate and the extract were combined and acidified with concentrated hydrochloric acid. Methanol was removed under reduced pressure and the residue was neutralized with aqueous sodium hydrogencarbonate. The resulting white precipitate was collected by filtration and boiled with 500 cm^3 of chloroform. The chloroform was removed from the extracts under reduced pressure and the residue was recrystallized from dioxane. The compound crystallized as colorless plates, mp 264 °C, yield 0.5 g.

Found: C, 74.78; H, 4.18; N, 9.76%. Calcd for $C_{18}H_{12}N_2O_2$: C, 75.01; H, 4.16; N, 9.72%.

Copper(II) Complex. 2,2′-Bi-8-quinolinol (0.1 g) was dissolved in minimum amount of hot dioxane and to this was added copper acetate monohydrate (0.065 g) in a dioxane–ethanol mixture (1:1). The mixture was heated on a water bath for 10 minutes and the resulting deep brown needles were collected by filtration and washed with methanol and dried at 100 °C under vacuum. The complex can be recrystallized from pyridine, but it is pure enough without recrystallization.

Found: C, 61.75; H, 2.87; N, 7.87; Cu, 18.22%. Calcd for $C_{18}H_{10}N_2O_2Cu$: C, 61.80; H, 2.88; N, 8.01; Cu, 18.16%.

Measurements. Molecular weight was determined by vaper pressure equilibrium method with a Hitachi Osmometer Type-115 using chloroform as a solvent. Infrared spectra were recorded in KBr disks with a Hitachi EPI-S2, and electronic spectra were taken with a Hitachi EPS-3T spectrophotometer. The magnetic moments were measured bv means of a recording magnetometer especially designed by Hirakawa *et al.*[10)]

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