Complex Formation of 3,7-Dihydroxy-1,5-diphenyloctahydro-1,5-diazocine with First Row Transition Elements (1)

W. P. Jensen, J. J. Worman, and O. D. Filbey

Department of Chemistry, South Dakota State University, Brookings, South Dakota 57006

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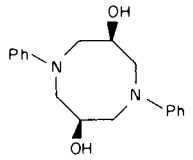
The ligand type (**1**) is interesting in that the 3,7-substituents can be varied to give complexes that are capable of quadrivalent, pentavalent and hexavalent coordination. Unlike similar ligands (2-7) which yield normal crystalline solid complexes with a number of transition metal salts, the title ligand type is unusual in that it complexes only with a couple of the transition metal ions (Cu (II) and Fe (III)).



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The electronic absorption spectrum of an ethanol solution of 3,7-dihydroxy-1,5-diphenyloctahydro-1,5-diazocine (**1**) and copper (II) at room temperature is shown in Figure 1. The geometry about the copper atom in the complex is designated as trigonal bipyramidal because of the similarity of the ligand field portion of the spectrum with those of complexes reported to be trigonal bipyramidal (6). It can be seen by the use of molecular models that this geometry is best achieved by the use of three of the potential donor sites on the ligand (most likely with two nitrogen atoms and one oxygen atom). The remaining two coordination positions could be occupied by anions or by solvent molecules (Figure II). Bonding of the fourth potential donor site of the ligand

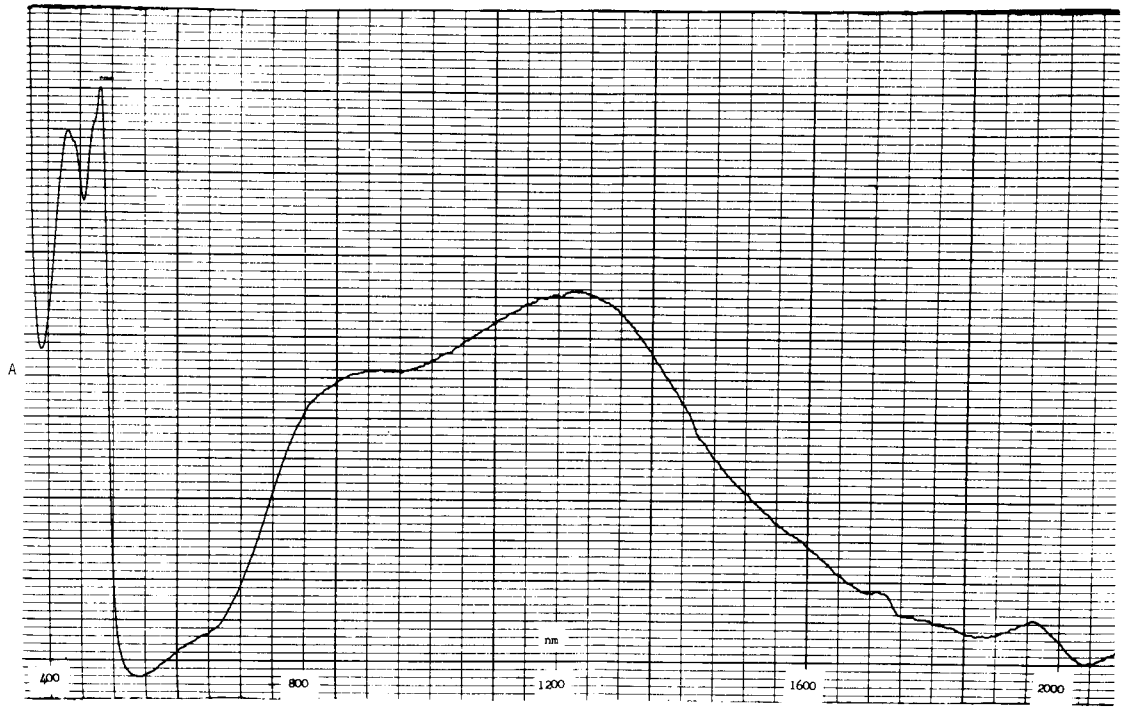

Figure 1. Visible - near infrared spectrum of the Copper(II)-I complex in ethanol.

is not likely due to the severe strain this would impose on the ligand. This hypothesis does not depend on the configuration of the ligand although the ligand is believed to be *cis* (7). The (II) oxidation state of copper in the Cu (II) ligand complex is demonstrated by the extreme line broadening of all of the nmr signals of the ligand

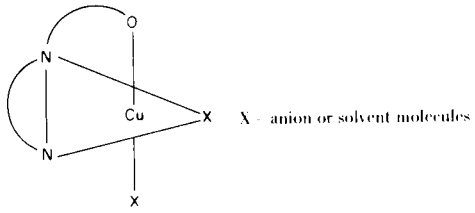

Figure II

hydrogens due to the paramagnetic interactions with Cu (II). The Cu (II) oxidation state in the complex is further demonstrated by the appearance of one epr signal with a g value of 2.01.

A continuous variation plot mixtures of copper (II) and I in ethanol at room temperature shows that only the 1:1 complex forms under these conditions (Figure III). Conductance data also indicate 1:1 complex formation. A continuous variation plot of a mixture of Fe (III) and **1** was inconclusive.

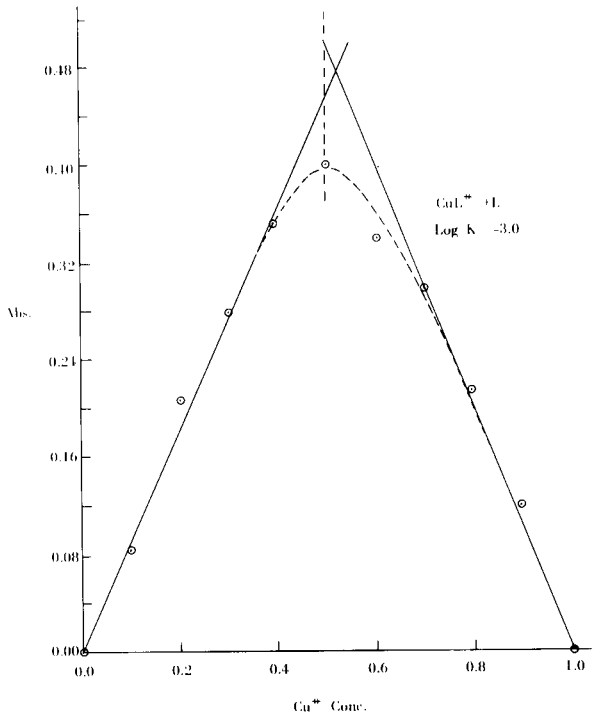

Figure III. Continuous variation plot of ethanol solutions of Copper(II) and I.

The specific reactivity of the ligand is demonstrated by the fact that it does not coordinate with Ni (II), Co (II), and (III), Mn (II), Cr (III), and V (III) as evidenced by no change in the original absorption spectrum of the ligand or metal salt upon mixing at room temperature or even under reflux conditions. Complex formation of the ligand, with Fe (III) is shown by the appearance of a charge transfer transition in the visible spectrum at a maximum of 610 nm.

Copper (II) and iron (III) solid complexes with the ligand were isolated from solution. The solid state electronic absorption spectra taken as either potassium bromide pellets or nujol mulls were similar to those of the complexes in solution indicating that the environment about the copper and iron atoms had not changed in going from solution to the solid state. Observations under a microscope and the absence of any x-ray powder diffraction lines indicate that the solids are amorphous. The mass spectra did not show the presence of parent ions and fragmentations were observed at m/e values greater than expected for the stoichiometries predicted in solution. This suggests a polymeric solid. This interpretation is substantiated by the fact that once the solids are removed from solution, it is extremely difficult to redissolve them in ethanol, even under reflux conditions.

An interesting feature of this ligand is the fact that it will react with Cu (II) or Fe (III) in the solid state when the compounds are mixed and ground gently in a mortar and pestle. Disappearance of x-ray powder diffraction lines of the starting materials as well as obvious color changes can only be interpreted as the formation of complex amorphous compounds.

Because of the complex nature of the ligand, rather unusual chelate structures can be obtained. Extension of these studies encompassing different substituents on the ligands is presently being pursued. The specific reactivity of the ligand toward certain transition metal ions is clearly demonstrated. The underlying reason for this specific reactivity awaits more detailed structural information.

EXPERIMENTAL

Solid complex species were prepared by two methods; by mixing stoichiometric amounts of the ligand and an anhydrous chloride metal salt as ethanol solutions (10^{-3}-10^{-5} *M*) and evaporating some of the solvent to precipitate the complexes; and by grinding powders of an anhydrous chloride metal salt and the ligand in a mortar and pestle. All attempts to crystallize the complexes were unsuccessful. In using the first preparative method copper salts reacted immediately with the ligand to form a complex while the iron salt required reflux conditions of up to 48 hours.

Solution state complexes were prepared by mixing ethanol solutions of the ligand and metal salt at concentrations varying between 10^{-3} and 10^{-5} *M*.

The ligand was prepared according to the procedure described by Gaertner (8).

Electronic absorption spectra of the solutions and solids were taken with a Beckman DK-2A spectrophotometer. The solid samples were prepared as potassium bromide pellets. Nmr data were taken with a Varian A-60 A spectrometer. Epr data were taken with a Varian E-3 spectrometer (9). X-ray diffraction data were taken by standard techniques.

Acknowledgment.

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(10) Epr and mass spectral data were taken at the University of Wyoming.