

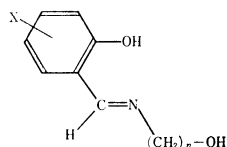
# New Types of Copper(II) Complexes with Subnormal Magnetic Moments

Shoichiro YAMADA and Kuniko YAMANOUCHI

*Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka*

(Received June 12, 1970)

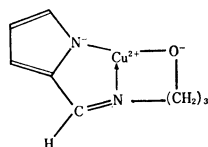
It is known that Schiff bases of a type represented by Formula I\*<sup>1</sup> form copper(II) complexes of a Cu(X-SAL.CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O) type with subnormal magnetic moments, which are considered to be due



Formula I

to an interaction between two copper(II) ions within the binuclear molecule.<sup>1,2)</sup> With Schiff bases of different series, we have recently succeeded in isolating crystals of new copper(II) complexes having subnormal magnetic moments.

A copper(II) complex shown by Formula II\*<sup>2</sup>

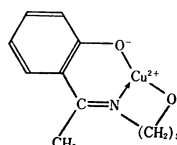


Formula II

was prepared as follows. An aqueous solution of copper(II) nitrate (0.005 mol) was added drop by drop to a solution of the Schiff base (0.01 mol) in ethanol, followed by addition of an aqueous solution of sodium carbonate (0.005 mol). After

the solution was stirred at 60°C for one hour, it was allowed to cool to room temperature. A brown precipitate was collected and recrystallized from benzene or chloroform to yield brown crystals. Found: C, 44.87; H, 4.70; N, 12.43%. Calcd for Cu(Pra.CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>OCu: C, 44.96; H, 4.72; N, 13.11%.

By a similar method except that 2-hydroxyacetophenone was used instead of pyrrole-2-carboxyaldehyde, a copper(II) complex shown by Formula III\*<sup>3</sup> was obtained as olive-colored crystals. This complex could also be obtained without sodium carbonate. Found: C, 52.04; H, 5.17; N, 5.53%. Calcd for Cu(Hap.CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), C<sub>11</sub>H<sub>13</sub>NO<sub>2</sub>Cu: C, 51.86; H, 5.14; N, 5.50%.



Formula III

The magnetic moments for Cu(Pra.CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O) and Cu(Hap.CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), which have been determined at room temperature to be 0.60 and 1.09 B. M., respectively, are significantly smaller than the spin-only moments expected for normal copper(II) complexes. The subnormal magnetic moments of these complexes are considered to be due to an antiferromagnetic interaction between copper(II) ions. One most probable structure may be a binuclear structure similar to that of the corresponding salicylideneiminato-complex.

It should be noted that similar methods using ethanol-amine instead of *n*-propanol-amine yielded compounds of a different type. Further study of copper(II) complexes with related ligands is now in progress.

\*<sup>1</sup> Abbreviated as X-SAL.Y-OH.

1) S. Yamada, Y. Kuge and K. Yamanouchi, *Inorg. Chim. Acta*, **1**, 139 (1967); S. Yamada, H. Nishikawa, Y. Kuge and K. Yamanouchi, *Sci. Rep.* (College of General Education, Osaka Univ.), **16**, 11 (1967).

2) M. Kato, Y. Muto, H. B. Jonassen, K. Imai and A. Harano, *This Bulletin*, **41**, 1864 (1968).

\*<sup>2</sup> Abbreviated as Cu(Pra.CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O).

\*<sup>3</sup> Abbreviated as Cu(Hap.CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O).