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The Copper(II) Complexes Distorted from a Planar Configuration

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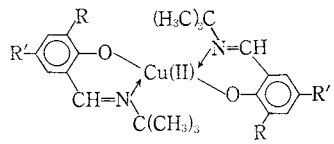
In the course of studies of the effects of bulky groups on the formation of dimeric copper(II) complexes with bridged alkoxy groups,[1] copper(II) complexes distorted from a planar configuration were synthesized.

With few exceptions, all X-ray analyses of the four coordinate copper(II) complexes have shown them to have a square planar arrangement of the donor atoms about the metal atom. We do not know of a purely tetrahedral copper(II) complex, but some distorted tetrahedral copper(II) complexes of Schiff bases from the substituted salicylaldehydes and the branched alkyl amines have been synthesized by Yamada and Nishikawa[2] and by Sacconi and Ciampolini.[3]

We synthesized the copper(II) complexes, I, II, and III, in which the bulky cyclohexyl or *t*-butyl groups are introduced not only in the amine component but also in the aldehyde portion. In these complexes, there must exist steric interactions between the bulky cyclohexyl or *t*-butyl group on the 3-position of the aldehyde portion and the bulky *t*-butyl group in the amine component. Two copper(II) complexes, I and III,[4] in chloroform showed a ligand-field band at 12200 cm^{-1}, while the complex II showed one at 12650 cm^{-1}. The square-planar copper(II) complexes of the $Cu(N)_2(O)_2$ type show absorption in the 17700 cm^{-1}



	R	R′
I	$C(CH_3)_3$	NO_2
II	cyclo-C_6H_{11}	CH_3
III	$C(CH_3)_3$	H

Fig. 1.

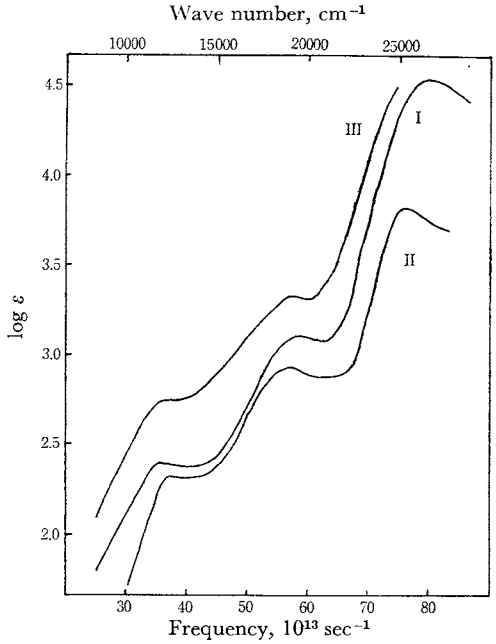


Fig. 2. Visible and near infrared spectra of the complexes, I, II, and III, in chloroform. The absorption curve of the complex, III, is arbitrarily plotted.

1) T. Inazu, H. Okawa, T. Inazu and T. Yoshino, This Bulletin, **42**, 2291 (1969).

2) S. Yamada and H. Nishikawa, *ibid.*, **36**, 755 (1963).

3) L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, **1964**, 276.

4) The complex, III, was not isolated in a pure crystalline state.

region,[5] and it is known that a ligand-field band shifts to a lower-wave-number region as distortion from a planar configuration increases.[2] Bis(*N*-*t*-butylsalicylideneiminato)copper(II), IV, which was considered to have a distorted tetrahedral configuration,[6] shows absorption in the 13000 cm^{-1} region.[2]

From these facts, the copper(II) complexes obtained here can be though to have a configuration much more distorted from the square-plane than the complex IV.

Experimental

The melting point is uncorrected. The visible and near-infrared spectra in a chloroform solution were measured on a Hitachi EPS-3T spectrophotometer.

***N*-*t*-Butyl-3-*t*-butyl-5-nitrosalicylideneimine.** To 500 mg of 3-*t*-butylsalicylaldehyde[1] in 1 m*l* of acetic acid, we added 0.5 m*l* of nitric acid (sp gr 1.38) at room temperature. After standing for a few minutes, the mixture was poured into water. To the yellow crystals thus obtained we added excess *t*-butylamine in methanol and refluxed the mixture for a few minutes. The yellow crystals thus obtained were recrystallized from methanol. Yield, 180 mg, mp 150—151°C.

Found: C, 64.70; H, 8.00; N, 9.97%. Calcd for $C_{15}H_{22}N_2O_3$: C, 64.72; H, 7.97; N, 10.07%.

Bis(*N*-*t*-butyl-3-*t*-bultyl-5-nitrosalicylideneiminato)copper(II), I. To 37.3 mg of *N*-*t*-butyl-3-*t*-butyl-5-nitrosalicylideneimine in 2 m*l* of hot methanol, we added 13.6 mg of copper(II) acetate monohydrate in 5 m*l* of methanol. Immediately violet-black crystals were obtained. The crystals were filtered out and washed with methanol. Yield, 20 mg.

Found: C, 58.45; H, 7.04; N, 9.03; Cu, 9.42%. Calcd for $C_{30}H_{42}N_4O_6Cu$: C, 58.28; H, 6.85; N, 9.06; Cu, 10.28%.

Bis(*N*-*t*-butyl-3-cyclohexyl-5-methylsalicylideneiminato)copper(II), II. Black crystals.

Found: C, 70.83; H, 8.50; N, 4.85; Cu, 10.58%. Calcd for $C_{36}H_{52}N_2O_2Cu$: C, 71.08; H, 8.62; N, 4.60; Cu, 10.45%.

5) A. von Kiss, G. Bacskai and P. Csokan, *J. Prakt. Chem.*, **160**, 1 (1942).

6) In this complex, the angle between the planes containing the coordinating atoms of each chelate group and the copper atom is 54° instead of the 90° expected for a truly tetrahedral configuration.[7]

7) T. P. Cheeseman, D. Hall and T. N. Waters, *J. Chem. Soc., A*, **1966**, 685.