

Preparation of a Dimeric Copper(II) Complex with Dithio α -Diketone

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Stilbenedithiol is a bidentate ligand containing two sulfur atoms. Several metal complexes with this ligand have been prepared by Schrauzer.¹⁾ Regarding the copper(II) complex, however, only bis(maleonitrile dithiolato)Cu(II)²⁾ and bis(toluene-3,4-dithiolato)Cu(II)³⁾ have been reported. In this paper, we will describe the preparation of a novel copper(II) complex with stilbenedithiol as a dithio α -diketone complex.

By using the benzoin- P_4S_{10} method,⁴⁾ a copper(II)-stilbenedithiolate complex was prepared through the reaction of the thiophosphoric ester of stilbenedithiol and an excess of copper(II) in benzene; a dark violet complex was thus isolated. This complex, recrystallized from dioxane, is soluble in dichloroethane, chloroform, and ethanol, and it was found by elementary analysis to have the formula of $Cu_2S_2(S_2C_2(C_6H_5)_2)_2$. (Found: C, 49.98; H, 3.22; S, 26.95 ± 3 ; Cu, 19.1%. Calcd for $Cu_2S_2(S_2C_2(C_6H_5)_2)_2$: C, 49.75; H, 2.99; S, 28.46; Cu, 18.08%). A molecular-weight determination by the use of the "Vapour Pressure Osmometer" showed that this compound was di-

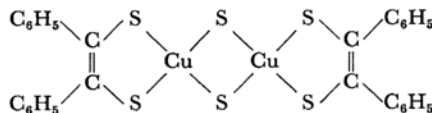


Fig. 1

meric (Found: 661, Calcd: 676) and had a sulfur-bridged structure, one similar to the dimeric compounds of iron(II)⁵⁾ and molybdenum.⁶⁾ The structure may be supposed, as is shown in Fig. 1, to be a dimeric copper(II)-stilbenedithiolate complex.

It was found that this complex is diamagnetic. The absorption spectrum of the complex in dichloromethane shows that all the electronic transitions are at slightly longer wavelengths than those of the monomer; this fact is probably due to the dithion resonance *via* the sulfur bridges.

In the infrared spectrum, the C=C band was observed at 1445 cm^{-1} ; this indicates about a 75% double-bond character, according to Schrauzer's relationship between the C=C stretching frequencies and the calculated % of the C=C character.⁵⁾ The peak at 328 cm^{-1} in the far-infrared region is probably to be assigned to the Cu-S stretching frequency. The detailed results will be reported shortly.

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5) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **88**, 4604 (1966).

6) G. N. Schrauzer and V. P. Mayweg, *ibid.*, **88**, 5174 (1966).