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THE STRUCTURE OF BIS(DIBENZYLAMINE)BIS(ETHYLTHIOACETATO)COPPER(II) ——SQUARE-PLANAR COPPER(II) COMPLEX

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The crystal and molecular structure of the title complex has been determined by the X-ray diffraction. The copper(II) atom is in a square-planar geometry, being coordinated with two nitrogen and two oxygen atoms. No atoms other than the phenyl group ones of the ligand exist in the axial direction of the CuN_2O_2 plane.

Although there are many copper(II) complexes having the chemical formula of CuL_4 (where L is a ligand), almost all of them are in a penta- or hexa-coordination geometry in crystals, including additional one or two weaker bonds from the axial direction of the CuL_4 plane.[1,8] In the cases of copper(II) β-diketonates, which are in a typical square-planar geometry, there is one each of the γ-carbon atom of another chelate about 3 Å above and beneath the CuO_4 plane.[2-6] A weak Cu-C bonding between them was proposed, although it was not decisive.[4,6] In the case of unidentate complexes of Cu(II), $Na[Cu^{II}(NH_3)_4][Cu^{I}(S_2O_3)_2]_2$,[7] and $Cu(C_5H_5NO)_4X_2$ (where X=BF_4 or ClO_4)[8] were reported as the rare examples of the pure square-planar ones. The title complex seems to be another example.

The title complex was synthesized as follows. Diaquabis(ethylthioacetato)-copper(II) (0.50 g, 1.5 mmol), and dibenzylamine (1.2 g, 6.0 mmol) were mixed with 5 cm^3 of benzene and were boiled until they dissolved. The supernatant fluid was mixed with 5 cm^3 of petroleum benzine, and it was left standing overnight in a desiccator over petroleum benzine. The deep violet product has precipitated (yield: 0.73 g, 70%). It was purified by reprecipitation: dissolved into benzine, containing the amine, and kept in a desiccator over petroleum benzine. Found: Cu, 9.19; C, 61.70; H, 6.35; N, 4.02%. Calcd for $CuC_{36}H_{44}S_2O_4N_2$: Cu, 9.12; C, 62.09; H, 6.37; N, 4.02%.

The reflectance spectra of the solid show the absorption maximum at 505 nm, and a shoulder at about 620 nm, while its benzene solution containing a large excess of dibenzylamine shows the absorption maximum at 560 nm (ε=160). Its magnetic moment measured by a Gouy balance (19° C) was 1.7_6 B.M. The same type of complexes were obtained using methylthio- or isopropylthioacetate of copper(II) and/or isoquinoline in place of the starting materials above mentioned.

The crystals are monoclinic, with the space group A2/a, a=19.235(8), b=11.944(2), c=17.137(5) Å, β=111.13(3)°, μ(Mo Kα)=0.592 mm^{-1}, F.W.=696.43, Z=4, D_m=1.26(2), and D_x=1.25 g cm^{-3}. The structure was solved by the heavy atom method, and refined to give R value of 0.055 (R_2=0.063), for 2090 $[|F_o|>3\sigma(|F_o|)]$

reflections from the 2188 independent ones obtained on a Philips 1100 automated four-circle diffractometer using Mo Kα radiation (λ=0.7107 Å).

A perspective drawing of the complex is shown in Fig.1. Selected inter-atomic distances and bond angles are shown in Table 1. The copper atom is at the center of symmetry, and occupies the center of an O_2N_2 square plane, although O(1)-Cu-N is 94.6(2)°. As the C(1)-O(2) bond extends to the direction much different from the Cu atom, and the Cu-S distance exceed 4.0 Å, both of O(2) and S atoms are not coordinated with the copper atom. On the other hand, the phenyl carbon atoms, C(21) and C(22) are in the axial direction of the CuO_2N_2 plane; 3.100(9), and 3.026(9) Å from Cu, respectively. There may be a weak bonding between them, like the Cu-C bond of the copper(II) β-diketonates.2-6) But, as almost no deformation of the phenyl group beyond the experimental error was observed, the interaction is likely weak. On the other hand, the interaction between both phenyl groups of a dibenzylamine molecule seems to be strong, and a phenyl group of the ligand comes to the axial position, like a *picket fence*, preventing the approach of another sulfur or oxygen atom of the ethylthioacetate ion to the coordination sphere of the central metal atom.

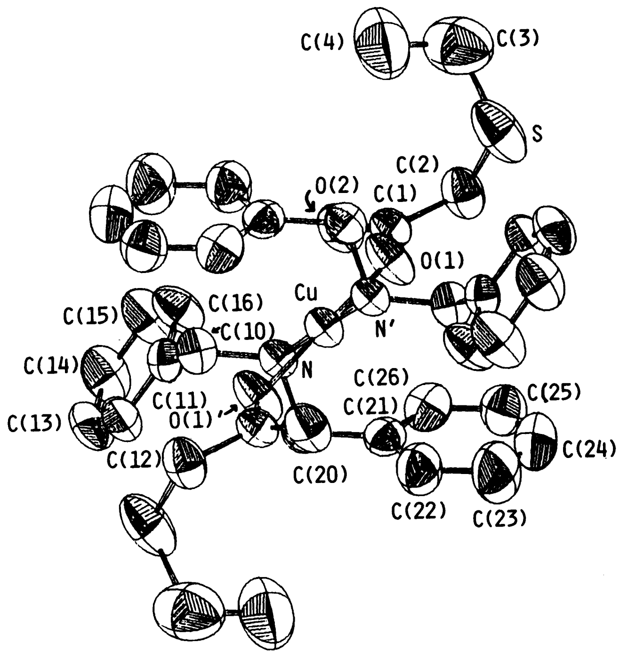

Fig.1. Perspective Drawing of the Complex.

Table 1. Interatomic Distances (ℓ/Å), and Bond Angles (ϕ/°).

Cu-O(1)	1.916(5)	Cu···O(2)	3.300(7)
Cu-N	2.026(6)	O(1)-C(1)	1.255(9)
O(2)-C(1)	1.221(7)	Cu···C(21)	3.100(9)
Cu···C(22)	3.286(9)	Cu···C(26)	3.895(11)
O(1)-Cu-N	94.6(2)	Cu-O(1)-C(1)	132.7(4)
O(1)-C(1)-O(2)	125.7(6)	O(1)-Cu···O(2)	39.9(2)
C(1)-O(2)···Cu	61.2(3)	O(1)-Cu···C(21)	85.1(2)
O(1)-Cu···C(22)	93.1(2)	N-Cu···C(21)	52.0(2)
N-Cu···C(22)	74.4(2)		

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