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THE STRUCTURE OF BIS(ISOPROPYLTHIOACETATO)TRIS(ISOQUINOLINE)COPPER(II) ——POTENTIALLY HEPTACOORDINATED COMPLEX

Yoshiyuki SATO, Akira OUCHI,* Yasuhiko YUKAWA,† and Toshio TAKEUCHI†

Department of Chemistry, College of General Education, The
University of Tokyo, Komaba 3-8-1, Meguro-ku, Tokyo 153
† Department of General Sciences, Faculty of Science and Technology,
Sophia University, Kioi-cho 7, Chiyoda-ku, Tokyo 102

The crystal and molecular structure of the title complex has been determined by the X-ray diffraction. The copper(II) atom is in a distorted pentagonal bipyramidal geometry, including two oxygen atoms of the both carboxylates from a little long distances. Sulfur atoms of the ligands do not coordinate to the central metal atom.

We have previously reported that in diaquabis(ethylthioacetato)copper(II)1) or in bis(isopropylthioacetato)copper(II) dihydrate,2) sulfide sulfur atoms of the ligands coordinate to the copper(II) atom forming chelate rings. When such alkylthioacetates of copper(II) were treated with some amine, CuL_2A_3 type adducts (where HL:alkylthioacetic acid, A:amine) were obtained. As the coordination geometry around copper(II) atom of them was expected to be interesting, the molecular structure of the title complex was solved by the X-ray diffraction.

The title complex was synthesized as follows. Bis(isopropylthioacetato)-copper(II) dihydrate(0.55 g, 1.5 mmol), and isoquinoline(1.0 g, 7.8 mmol) were boiled with 5 cm^3 of benzene, and dissolved. The supernatant fluid was mixed with 8 cm^3 of ligroine and was left standing for several hours until the blue crystals were precipitated (yield: 0.7 g, 65%). It was recrystallized from toluene-ligroine (1:1.5=v/v) containing about 2 mol dm^{-3} of isoquinoline. Found: Cu, 9.09; C, 62.07; H, 5.46; N, 5.84%. Calcd for $CuC_{37}H_{39}S_2O_4N_3$: Cu, 8.86; C, 61.95; H, 5.48; N, 5.86%. The reflectance spectra of the solid, and the absorption spectra of the benzene solution containing large excess of isoquinoline show the absorption maxima at 650 and 668 nm, respectively. Its dilute solution in benzene was green in color, and its absorption maximum appeared at 730 nm, which resembled that of $Cu_2(H_2O)_2(CH_3CO_2)_4$.3) Magnetic moment measured by a Gouy balance at 15 °C was 1.82 B.M. The same type of complexes were obtained using methylthio- or ethylthioacetate of copper(II) and/or pyridine in place of the starting materials abovementioned, too.

The crystals are triclinic, with the space group $P\bar{1}$, a=11.550(10), b=16.912(6), c=9.792(9) Å, α= 100.32(5), β=109.96(13), γ=79.50(5)°, μ(Mo Kα)=0.553 mm^{-1}, F.W.=717.41, Z=2, D_m=1.36(2), and D_x=1.34. The structure was solved by the heavy atom method, and refined to give R value of 0.0781 for 3404 [$F_o>3\sigma(F_o)$] reflections from the 3832 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 bond lengths and bond angles are shown in Fig. 2, and Table 1.

As shown in Fig. 2, copper(II) atom is approximately in a pentagonal bipyramidal geometry, where N(32) and N(42) are in the axial direction. The least-squares plane through the atoms Cu, O(11), O(12), O(21), O(22), and N(52) is shown as $0.5509X+0.6316Y-0.5455Z+3.3120=0.0$ (where X,Y,Z are coordinates in Å), and the distances from the plane are: Cu, 0.026; O(11), -0.003; O(12), 0.002; O(21), 0.052; O(22), -0.036; N(52), -0.038 Å. Dihedral angles between the pentagone and those of isoquinoline molecules are: (32), 80.5; (42), 86.7; (52), 14.0° (where the number means each isoquinoline molecule including the numbering N atom).

Table 1. Bond Angles (ϕ/°).

O(11)-Cu-N(52)	90.2(2)	N(42)-Cu-N(32)	163.7(3)
O(21)-Cu-N(52)	88.6(2)	N(32)-Cu-N(52)	94.2(3)
O(11)-Cu-O(12)	55.1(2)	N(32)-Cu-O(11)	88.0(3)
O(11)-Cu-O(21)	178.8(2)	N(42)-Cu-O(11)	90.7(3)
O(21)-Cu-O(22)	41.4(2)	N(32)-Cu-O(21)	92.1(3)
O(12)-Cu-O(22)	84.7(2)	N(42)-Cu-O(21)	89.6(3)
N(42)-Cu-N(52)	102.0(3)		

This kind of the structure was found only in dinitratotris(pyridine)copper(II),[4] and no example has been reported about the carboxylato complexes of copper(II). Although diacetatotris(pyridine)-copper(II) reported by Anzenhofer[5] may have the similar type type of structure, his report shows a different type of figure for the compound.

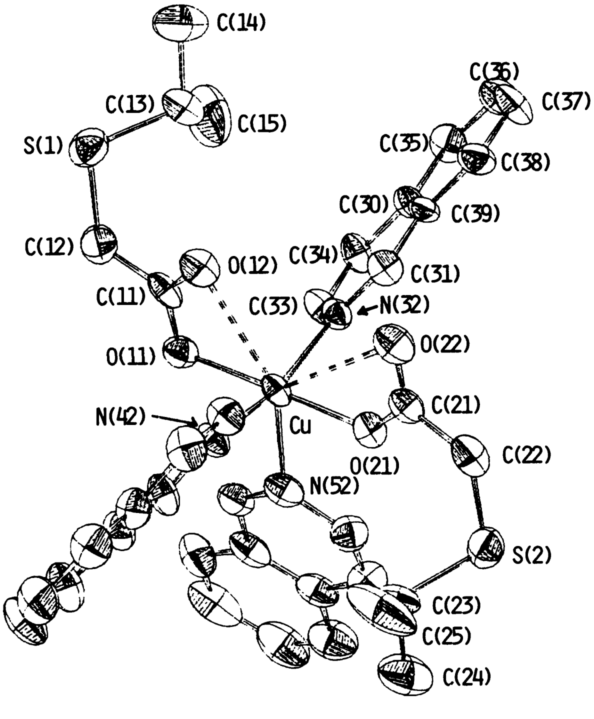

Fig. 1. Perspective Drawing of the Complex.

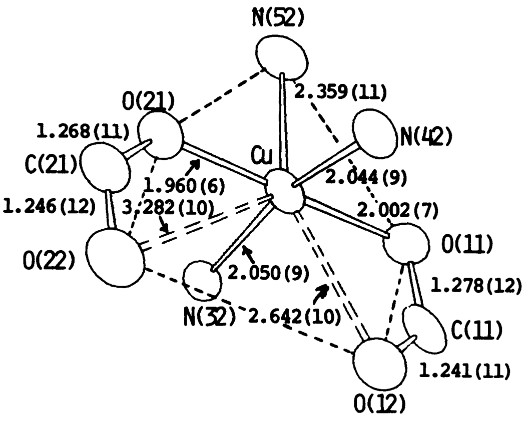

Fig. 2. Selected Bond Lengths (l/Å).

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