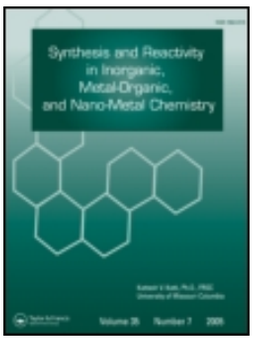

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# DIRECT SYNTHESIS AND PROPERTIES OF BINUCLEAR COPPER(II) COMPLEXES

**Ruina Yang,*[,1] Dongmei Wang,[1] Aiyan Kuang,[1] Yingfan Liu,[1] and Douman Jin[2]**

[1]Henan Institute of Chemistry, Zhengzhou 450002, P. R. China
[2]State Key Laboratory of Coordination Chemistry, Nanjing University 210093, P. R. China



## ABSTRACT

At room temperature, dibenzoyl peroxide undergoes an oxidative addition reaction with metallic copper powder and the relevant ligands afford binuclear copper(II) complexes, $[Cu(OOCC_6H_5)_2L]_2$, L = pyridine-2,6-dicarboxylic acid ($L^1$), THF ($L^2$), 3-aminopyridine ($L^3$), 4-aminopyridine ($L^4$), 2-methylpyridine ($L^5$), 2,6-dimethylpyridine ($L^6$) and 2-aminothiazol ($L^7$). These complexes were further characterized by physico-chemical and spectroscopic methods. The structure of complex (**7**) has been determined by a single-crystal X-ray analysis. Each copper(II) ion is coordinated by two bridging bidentate benzoates and one L (as defined above) ligand to form dimeric binuclear molecules.

*Corresponding author. E-mail: yangrn@371.net

## INTRODUCTION

Binuclear copper(II) complexes are very important in coordination chemistry and catalytic reactions. Certain copper complexes have been shown to have unusual chemical properties of importance in such diverse areas as oxygen transfer, oxidative addition and homogenous hydrogenation[1]. Oxidative addition reactions are key steps in the activation of σ bonds in a great number of catalytic processes[1]. Copper(II) complexes are widely used as catalysts in the decomposition of disubstituted peroxides[1]. To obtain insight into the correlation between the structure and nature of copper catalysts, low-molecular weight coordination compounds may be prepared[2]. The electronic structure and bonding at the copper catalysts can be profitably pursued by studying model complexes. These considerations prompted efforts to develop easy methods for the synthesis of binuclear copper(II) complexes which would possess novel coordination chemistry. Our aim is to investigate oxidative additions of the O-O bond in dibenzoyl peroxide to metallic copper. Since the investigation of dinuclear compounds of transition metals constitutes a field of continuing research interest, this report concerns an oxidative preparation method of copper(II) complexes. In this work we first prepared seven binuclear copper(II) compounds by oxidative addition reactions. X-ray structure analysis of the binuclear copper(II) complex $[Cu(C_3H_4N_2S)(OOCC_6H_5)_2]_2$ is reported. It also describes a detailed study of the spectroscopic properties of the title compounds.

## EXPERIMENTAL

### Physical Measurements

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification for the preparation of the complexes. Elemental analyses were performed on an ERBA-1106 instrument. Copper was determined using a JA96-975 ICP-AES (Inductively Coupled Plasmas Atomic Emission Spectrometer). Molecular weight determinations were made in chloroform solutions at 25 °C using a CORONA-117 analyser. IR spectra were recorded on a Nicolet 170SX IR spectrophotometer in Nujol or CsI. TGA was carried out at a heating rate of 5 °C/min on a PE-TGS-2 thermal analyzer. Conductivity measurements were carried out in acetone solutions thermostatted at 25 °C using a DDS-11A analyser. Electronic spectra were recorded with a Hitachi 330 spectrophotometer (chloroform solution). Magnetic measurements were carried

out on polycrystalline samples on a pendulum-type magnetometer equipped with a nitrogen continuous-flow cryostat working in the 75–300 K range. MCD spectra were recorded on a JASCO-J20C automatic spectropolarimeter (magnetic field: 7000 Gauss, pool length: 0.5 cm, scale: 0.002/cm).

### Synthesis of the Complexes

2-Aminothiazol (1 mmol, 100 mg) was added to a mixture of dibenzoyl peroxide (1 mmol, 242 mg) and copper powder (1 mgatom, 63.5 mg) in a mixture of methanol (30 mL) and acetone (30 mL). The mixture was stirred for 48 h at room temperature. The resulting blue solution was filtered and left to yield blue crystals of compound (**7**). The complexes (**1**) to (**6**) may be prepared by similar methods, except for complex (**2**) which was obtained in a mixture of methanol and THF (1:1).

### X-Ray Data Collection[3]

A blue prismatic crystal of the complex (**7**) of dimensions $0.10 \times 0.15 \times 0.15$ mm was selected and mounted on an automatic Enraf-Nonius CAD-4 four-circle diffractometer. Intensities were collected with a graphite monochromator and $MoK_\alpha$ radiation ($\lambda = 0.71073$ Å), using the $\omega-2\theta$ scan technique. 6369 independent reflections were collected in the range of $1^\circ < \theta < 25^\circ$; a total of 3429 observable reflections with $[I \geq 3\sigma(I)]$ were used in the succeeding refinements. Crystallographic data are as follows: monoclinic, space group $P2_1/n$, a = 10.685(1) Å b = 19.028(6) Å, c = 17.046(9) Å, $\beta = 96.49(3)^\circ$, $V = 3443.4$ Å$^3$, $Z = 4$, $D_{(calcd.)} = 1.565$ Mg/m$^3$, $R = 0.046$, $R_w = 0.053$.

## RESULTS AND DISCUSSION

### Preparation of the Complexes

Dibenzoyl peroxide and the ligands [pyridine-2,6-dicarboxylic acid ($L^1$), THF ($L^2$), 3-aminopyridine ($L^3$), 4-aminopyridine ($L^4$), 2-methylpyridine ($L^5$), 2,6-dimethylpyridine ($L^6$), 2-aminothiazol ($L^7$)] reacted with metallic copper powder at room temperature giving blue solutions, the insoluble copper powder is observed to dissolve rapidly. After a few days,

blue crystals were deposited in good yield. This indicates the formation of the copper(II) compounds. The mechanism of the oxidative

$$Cu + (C_6H_5COO)_2 + C_3H_4N_2S\ (L^7) \rightarrow [Cu(C_3H_4N_2S)(OOCC_6H_5)_2]_2$$

addition reaction is probably stepwise as the benzoyl radical reacts with Cu to give copper(I) benzoate which then, in a subsequent reaction with a further benzoyl radical, results in the binuclear copper(II) carboxylate complex. These processes may be regarded as involving successive oxidations of Cu, ending with the copper(II) carboxylate compounds.

According to colour changes in the process of producing the title complexes and the obtained results, metallic copper powder has been oxidized to form Cu(II) complexes. Therefore, the direct use of metallic copper powder is characteristic of the present synthetic method. Molecular weights were determined in $CHCl_3$ solution. The compounds were soluble enough for measurements. Results are quite reproducible and seem to be scarcely influenced by variation of concentrations. In the case of the present complexes, molecular weight measurements give values strongly supporting the existence of the expected binuclear species. The complexes are stable in air at room temperature. They are easily soluble in acetone and methanol, and sparingly soluble in benzene and hexane. Their molar conductivities in acetone show that the title complexes are non-electrolytes. Thus, the binuclear Cu(II) complexes with coordinated benzoate groups may be obtained in high yields through oxidative addition reactions. The elemental analyses of the title complexes agreed well with their formulas (Table I).

## IR and Electronic Spectra

Benzoate may coordinate to a metal ion in one of the following modes: unidentate, bidentate or bridging. IR data (Table II) show the existence of bridging benzoato groups by the observation of characteristic absorption bands (1600–1400, 950–700, 500–600 $cm^{-1}$)[4]. The IR spectra of the title complexes are consistent with other known bridged carboxylate metal complexes as determined by the position and separation between the antisymmetric ($\nu_{as}$) and symmetric ($\nu_s$) stretches of the carboxylate group[5,6]. These complexes exhibit carboxylate stretches at 1570–1585 and 1400–1405 $cm^{-1}$, respectively, where $\Delta\nu$ ($\nu_{asym}-\nu_{sym}$) is 170–182 $cm^{-1}$, consistent with a bridging mode[5]. In the range 950–700 and 500–600 $cm^{-1}$, they display the characteristic absorption bands of $\delta$(COO) and $\pi$(COO), respectively. These

***Table I.*** Elemental Analysis Data of the Complexes

| Complexes | Empirical Formulas | Found (calcd.)% C | H | N | Cu | Color | Conductivity ($S \cdot cm^2 \cdot mol^{-1}$) | Mw (calcd.) | Yield (%) | Mp ( °C) or Dec. point |
|---|---|---|---|---|---|---|---|---|---|---|
| (**1**) $[CuL^1(OOCC_6H_5)_2]_2$ | $C_{42}H_{30}O_{16}N_2Cu_2$ | 53.11 (57.33) | 3.36 (3.17) | 2.76 (2.96) | 13.5 (13.4) | green | 4.5 | 943 (945) | 69 | 232 |
| (**2**) $[CuL^2(OOCC_6H_5)_2]_2$ | $C_{36}H_{36}O_{10}Cu_2$ | 57.01 (57.22) | 4.56 (4.77) | | 16.5 (16.8) | blue | 3.8 | 753 (755) | 76 | 180 |
| (**3**) $[CuL^3(OOCC_6H_5)_2]_2$ | $C_{38}H_{32}O_8N_4Cu_2$ | 57.23 (57.07) | 4.11 (4.00) | 7.25 (7.01) | 15.6 (15.9) | green | 2.6 | 798 (799) | 82 | 186 |
| (**4**) $[CuL^4(OOCC_6H_5)_2]_2$ | $C_{38}H_{32}O_8N_4Cu_2$ | 56.89 (57.07) | 3.88 (4.00) | 6.91 (7.01) | 15.7 (15.9) | green | 3.1 | 797 (799) | 75 | 201 |
| (**5**) $[CuL^5(OOCC_6H_5)_2]_2$ | $C_{40}H_{34}O_8N_2Cu_2$ | 59.99 (60.22) | 4.12 (4.27) | 3.28 (3.51) | 15.6 (15.9) | blue | 1.9 | 796 (797) | 66 | 220 |
| (**6**) $[CuL^6(OOCC_6H_5)_2]_2$ | $C_{42}H_{38}O_8N_2Cu_2$ | 61.22 (61.09) | 4.51 (4.61) | 3.18 (3.39) | 15.1 (15.4) | blue | 3.3 | 823 (825) | 71 | 229 |
| (**7**) $[CuL^7(OOCC_6H_5)_2]_2$ | $C_{34}H_{28}O_8N_4S_2Cu_2$ | 50.21 (50.31) | 3.38 (3.45) | 6.96 (6.90) | 15.3 (15.6) | blue | 2.2 | 810 (811) | 63 | 171 |

***Table II.*** Observed Spectra and Thermogravimetric Analysis Data of the Complexes

| Complexes | $\nu_{as}$(COO) | $\nu_{s}$(COO) | $\lambda$ (nm) ($\epsilon$ $M^{-1}\cdot cm^{-1}$) | g | $-2J$ ($cm^{-1}$) | F($10^{-5}$)[a] | Temp. ( °C) | Leaving Group | Wt. Expt.% (Wt. Calc. %) |
|---|---|---|---|---|---|---|---|---|---|
| (**1**) | 1580 s | 1402 m | 680 (188), 370 sh | 2.06 | 202.06 | 3.48 | 200–288 | $L^1$ | 34.1 (35.3) |
| (**2**) | 1575 s | 1405 m | 675 (192), 375 sh | 2.10 | 202.34 | 1.2 | 186–289 | $L^2$ | 18.6 (19.1) |
| (**3**) | 1570 s | 1400 m | 682 (201), 380 sh | 2.08 | 202.4 | 3.6 | 170–313 | $L^3$ | 22.1 (23.5) |
| (**4**) | 1581 s | 1400 m | 685 (176), 382 sh | 2.10 | 255.0 | 5.6 | 175–303 | $L^4$ | 22.3 (23.5) |
| (**5**) | 1572 s | 1405 m | 679 (184), 370 sh | 2.06 | 208.18 | 2.9 | 227–302 | $L^5$ | 21.9 (23.3) |
| (**6**) | 1585 s | 1403 m | 687 (191), 378 sh | 2.00 | 381.96 | 0.7 | 190–291 | $L^6$ | 24.6 (25.9) |
| (**7**) | 1570 s | 1400 m | 678 (203), 373 sh | 2.06 | 306.4 | 0.3 | 156–290 | $L^7$ | 23.9 (24.7) |

[a]2J is the exchange coupling constant; F is the quality factor defined as $F = \sum(\chi_0 - \chi_c)^2/\chi_o$.

are typical of a bridging coordination of benzoate[7,8]. They are consistent with the results of the crystal structure of the complex.

The observed absorption band maxima in the electronic spectra (Table II), as well as the IR spectra, agreed with those in the literature[9]. The wide bands (675–685 nm) belong to d-d transitions of copper(II), while a shoulder band (370–382 nm) is characteristic of the bridging system with antiferromagnetic interaction[9].



## Thermal Analysis of the Complexes

The TG-DTA thermogram of complex (**5**) reveals that the pyrolitic decomposition takes place in two steps. For example, the first one corresponds to a weight loss of 21.9% and is probably due to decomposition of the ligand 2-methylpyridine (loss of weight calculated: 23.3%). The decomposition process is confirmed by a strong endothermic peak at 227–302 °C. The second step, in the 302–680 °C temperature range, corresponds to a pronounced weight loss due to the combustion of the organic matter, giving CuO as final residue (determined by X-ray powder patterns; experimental weight of residue: 21.6%, calcd. 20.0%). The decomposition pattern of complex (**1**) is shown in Fig. 1. The first step is due to the loss of pyridine-2,6-dicarboxylic acid (loss of weight calculated: 35.3%, found: 34.1%). A strong endothermic peak exists in the 200–288 °C temperature range. The second step is due to the combustion of the organic matter, giving CuO as final residue.

## Magnetic Properties of the Complexes

The magnetic parameters for the compounds reveal their similarity (Table II). Temperature-dependent magnetic susceptibility data for the seven complexes have been measured from 300 K down to 100 K. The $\mu_{eff}$ values are *ca.* 2.0 B.M. for these complexes at room temperature. Upon cooling down from 25 °C, the values decrease continuously for all seven complexes, thus indicating a strong antiferromagnetic interaction between the copper(II) atoms in the dimeric or dinuclear structures. Assuming isotropic exchange, the exchange Hamiltonian is $H = -2JS_1S_2$ with $S_1 = S_2 = 1/2$, and the magnetic susceptibility per cation is given by the following equation:

$$\chi_m = (2N\beta^2g^2/KT)[3 + \exp(-2J/KT)]^{-1} + N_a$$

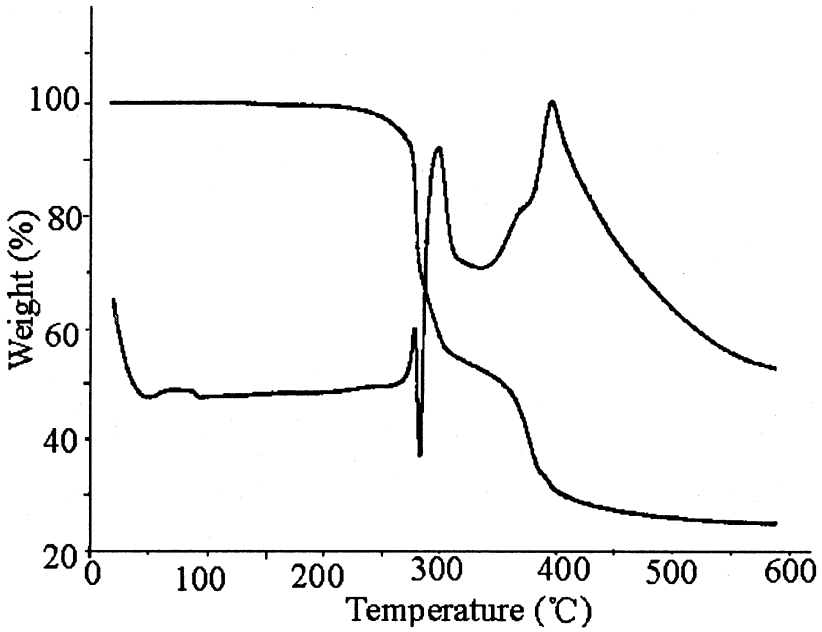


*Figure 1.* TG-DTA curves of complex (**1**).

where N, g, $\beta$, K are Avogadro's constant, g factor, Bohr magneton and Boltzman constant, respectively, $N_a = 1.50 \times 10^{-9}$ $m^2/mol$. J is the exchange integral, if $J < 0$, there is ferromagnetic interaction between magnetic metal ions, for $J < 0$, there is antiferromagnetic interaction between magnetic metal ions. Least-squares fitting of experimental magnetic data with the above equation gave the superexchange parameters (Table II), where $F$ is the quality factor defined as $F = \sum(\chi_o - \chi_c)^2/\chi_o$. The value of the superexchange parameter for the title compounds should be considered as normal, taking into account the structural and magnetic data found in the literature for binuclear copper(II) complexes[7–9].

There have been several attempts to correlate the magnitude of J with structural parameters (related with the coordination sites and with the bridging groups) in the $[Cu_2(RCOO)_4]$ cluster and/or with the donor properties of both carboxylate and axial ligands, but none of these efforts has proved successful. In this sense, it must be pointed out that the estimated uncertainties in the J values (*ca.* 5–10%) are of the same order of magnitude as the variations of that parameter within a series of related compounds (i.e. for the tetraacetatodicopper(II) adducts the J values fall in the range 285–325 $cm^{-1}$). However, in the case of tetrabenzoate derivatives the values

of J span a much wider range (from 100 to 390 $cm^{-1}$). An inspection of the structural parameters for these compounds indicates that no magneto-structural correlation can be established. In fact, some outstanding parameters involving the metal atoms such as the Cu-Cu or Cu-$O_{basal}$ distances and the C-O-Cu angle are not correlated with copper(II)-copper(II) interaction[9,10]. On the other hand, the structural differences in the bridging network are substantially within the experimental error[10].

## Magnetic Circular Dispersion Spectra (MCD)

In general, the interaction between monocolor circular light and a substance may be described by two absorption coefficients. The difference between the two absorption coefficients is the circular dispersion spectrum. The magnetic interactions between antiferromagnetic substances may be explored through the Faraday parameter of magnetic circular dispersion spectra. Experimental data for (**3**): $4 \times 10^{-3}$ M (acetone solution), $\lambda_{max} = 520$, 280 nm, $[\theta]_M = -7.14 \times 10^{-2}, +4.71 \times 10^{-2}$, $B = +5.20 \times 10^{-5}, -3.768 \times 10^{-4}$. Experimental data for (**7**): $1 \times 10^{-3}$ M (acetone solution, Fig. 2), $\lambda_{max} = 500$, 290 nm, $[\theta]_M = -5.71 \times 10^{-2}, +6.28 \times 10^{-2}$, $B = +5.18 \times 10^{-4}, -1.906 \times 10^{-4}$, θ: ovality/Gauss-mol. The Faraday parameter (B) was calculated from the following equation:

$$\int_0^\infty \text{band}([\theta]_M/\nu)d\nu = -33.53(B + C/KT)$$

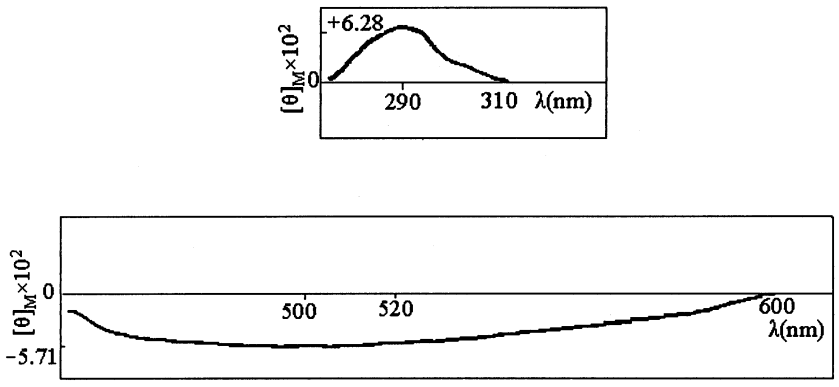


***Figure 2.*** MCD spectrum of complex (**7**).

MCD data of the complexes (**3**) and (**7**) show a positive peak at $\sim$290 nm in the UV region and a negative peak at $\sim$500 nm in the visible region. The former is attributed to the $A_{1g} \rightarrow {}^1B_{2u}$ transition of a benzenoid structure. The negative MCD peak ($\sim$500 nm) results from $d_{xy} \rightarrow d_{x^2-y^2}$ transitions. The blending of 3d and 4p orbitals give rise to non-zero rotation strength with magnetic field. MCD of the complexes only bring about the Faraday parameter (B). Faraday parameters (A) are absent. The Faraday parameter (A) is related to the magnetic moment. The absence of A showed antiferromagnetic interaction between the copper atoms[11]. The results confirm the formation of binuclear complexes.



## Crystal Structure

Figure 3 illustrates the conformation of the molecule. Selected bond distances and angles of complex (**7**) are listed in Table III, supplementary data are collected in Table IV.

There have been many structural reports concerning bridged binuclear copper(II) compounds that are similar to the present complexes[7–9]. The carboxylate bridged Cu$\cdots$Cu distance of the present compound is found to be 2.678(1) Å, which is comparable to that in tetrakis (benzoate)bis(triphenylphosphine oxide)dicopper(II), 2.657(1) Å[12]. The average C-O distances in the complex are not significantly different, 1.254 Å, and possess values comparable to those in other benzoate-bridging dicopper complexes[6]. All other bond distances and angles are within normal ranges.

In the binuclear copper(II) complexes, the Cu atom is coordinated by five atoms: four oxygens belonging to bridging carboxyl groups, and one N atom of 2-aminothiazol. Two benzoate groups and two 2-aminothiazol ligands are, respectively, located on the opposite sides to minimise repulsion between the ligands.

Complex (**7**) has the expected dimeric form bridged *via* carboxylate groups. Each copper(II) shows a five-fold coordination in the form of a distorted square pyramid with the four O atoms of the bridging carboxyl groups in the basal plane and the N atom of a 2-aminothiazol molecule at the apex. The sums of angles around each copper center, of $\measuredangle$ O(1)-Cu(1)-O(7) (88.1°), $\measuredangle$ O(7)-Cu(1)-O(3) (88.5°), $\measuredangle$ O(3)-Cu(1)-O(5) (89.6°), $\measuredangle$ O(5)-Cu(1)-O(1) (91.0°) and $\measuredangle$ O(2)-Cu(2)-O(8) (89.4°), $\measuredangle$ O(8)-Cu(2)-O(4) (91.3°), $\measuredangle$ O(4)-Cu(2)-O(6) (88.6°), $\measuredangle$ O(6)-Cu(2)-O(2) (87.9°) is 357.2° (near 360°). Four oxygen atoms lie in the basal plane with average interatomic distances of Cu-O of 1.974 Å, and similar values have been observed in tetrakis(benzoate)bis(triphenylphosphine oxide)dicopper(II)

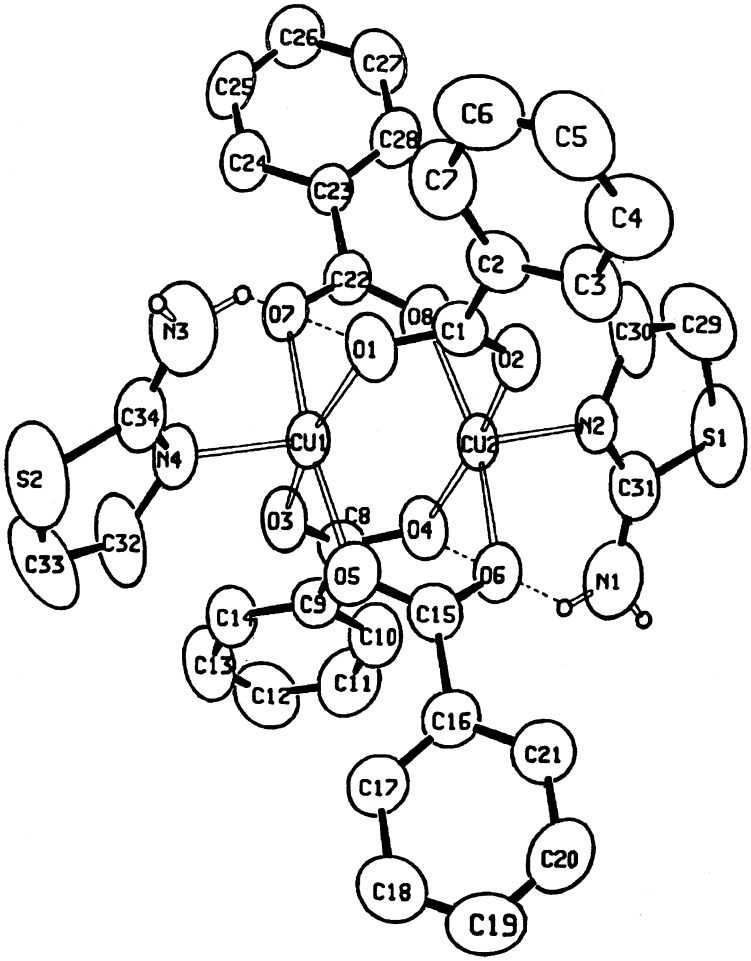


***Figure 3.*** Molecular structure of $[Cu(C_3H_4N_2S)(OOCC_6H_5)_2]_2$.

***Table III.*** Selected Bond Lengths (Å) and Angles (°) for Complex (**7**)

| | | | | | |
|---|---|---|---|---|---|
| Bond distances | | | | | |
| Cu(1)-Cu(2) | 2.678(1) | Cu(1)-O(1) | 2.011(5) | Cu(1)-O(3) | 1.967(5) |
| Cu(1)-O(5) | 1.961(6) | Cu(1)-O(7) | 1.956(5) | Cu(1)-N(4) | 2.162(6) |
| Cu(2)-O(2) | 1.945(5) | Cu(2)-O(4) | 1.952(5) | Cu(2)-O(6) | 1.978(5) |
| Cu(2)-O(8) | 2.024(5) | Cu(2)-N(2) | 2.135(6) | | |
| Bond angles | | | | | |
| Cu(2)-Cu(1)-O(1) | | 80.2(1) | Cu(2)-Cu(1)-O(3) | | 83.2(2) |
| Cu(2)-Cu(1)-O(5) | | 80.9(2) | Cu(2)-Cu(1)-O(7) | | 89.6(2) |
| Cu(2)-Cu(1)-N(4) | | 170.4(2) | O(1)-Cu(1)-O(3) | | 163.1(2) |
| O(1)-Cu(1)-O(5) | | 91.0(2) | O(1)-Cu(1)-O(7) | | 88.1(2) |
| O(3)-Cu(1)-N(4) | | 100.0(2) | O(5)-Cu(1)-O(7) | | 170.4(2) |
| O(5)-Cu(1)-N(4) | | 90.1(2) | O(7)-Cu(1)-N(4) | | 99.5(2) |
| Cu(1)-Cu(2)-O(2) | | 86.9(1) | Cu(1)-Cu(2)-O(4) | | 83.6(1) |
| Cu(1)-Cu(2)-O(6) | | 85.8(2) | Cu(1)-Cu(2)-O(8) | | 77.4(4) |
| Cu(1)-Cu(2)-N(2) | | 168.1(2) | O(2)-Cu(2)-O(4) | | 170.1(2) |
| O(2)-Cu(2)-O(6) | | 87.9(2) | O(2)-Cu(2)-O(8) | | 89.4(2) |
| O(2)-Cu(2)-N(2) | | 97.5(2) | O(4)-Cu(2)-O(6) | | 88.6(2) |
| O(4)-Cu(2)-O(8) | | 91.3(2) | O(4)-Cu(2)-N(2) | | 91.6(2) |

(av. 1.968 Å)[12]. The nearest neighbours of the copper atom are the four oxygen atoms of the bridging benzoate ligands in a square-planar arrangement. A square-based pyramidal arrangement about the copper atom is completed by the nitrogen of the 2-aminothiazol ligand at 2.135(6)–2.162(6) Å from the copper atom. The apical N atom is slightly displaced from the regular position and the N-Cu-O angles are between 90.1° and 100.0° [See also the Cu(2)-Cu(1)-N(4) and Cu(1)-Cu(2)-N(2) angles in Table III]. The Cu(1) and Cu(2) atoms lie 0.164(5) Å and 0.168(5) Å, respectively, out of the least-squares plane defined by the four oxygen atoms. The eight-membered ring of Cu(1) O(1) C(1) O(2) Cu(2) O(4) C(8) O(3) (the sum of angles is 1078.7°) and Cu(1) O(5) C(15) O(6) Cu(2) O(8) C(22) O(7) (the sum of angles is 1079.6°) are in the basal plane conformation. The dihedral angle is 89.9°.

There are intramolecular hydrogen bonds in complex (**7**). The lengths and angles of hydrogen bonds are O(4)-H(01) (3.06 Å), O(1)-H(03) (2.95 Å), N(3)-H(03)-O(1) (138.2°) and N(1)-H(01)-O(4) (125.6°). The bond distances of C(1)-O(1) (1.272 Å) and C(8)-O(4) (1.270 Å) are longer than other C-O bonds (1.229–1.267 Å) because of formation of hydrogen bonds.

***Table IV.*** Positional Parameters and Their Estimated Standard Deviations of Complex (**7**)

| Atom | x | y | z | B(Å$^2$) |
|---|---|---|---|---|
| Cu(1) | 0.09523(9) | 0.06990(5) | 0.32622(5) | 3.17(2) |
| Cu(2) | 0.00027(9) | 0.16995(5) | 0.22615(5) | 3.08(2) |
| O(1) | 0.0227(5) | 0.1347(3) | 0.4026(3) | 4.4(1) |
| O(2) | −0.0493(5) | 0.2189(3) | 0.3180(3) | 4.0(1) |
| O(3) | 0.1372(5) | 0.0245(3) | 0.2289(3) | 4.1(1) |
| O(4) | 0.0690(5) | 0.1114(3) | 0.1473(3) | 4.2(1) |
| O(5) | 0.2451(5) | 0.1295(3) | 0.3266(3) | 4.7(1) |
| O(6) | 0.1671(5) | 0.2155(3) | 0.2474(3) | 4.2(1) |
| O(7) | −0.0670(5) | 0.0213(3) | 0.3123(3) | 4.0(1) |
| O(8) | −0.1476(5) | 0.1040(3) | 0.2296(3) | 4.0(1) |
| C(1) | −0.0274(7) | 0.1942(4) | 0.3854(4) | 3.6(2) |
| C(2) | −0.0648(8) | 0.2369(4) | 0.4530(4) | 4.1(2) |
| C(3) | −0.0587(9) | 0.3080(4) | 0.4467(5) | 5.6(2) |
| C(4) | −0.088(1) | 0.3483(6) | 0.5172(5) | 8.1(3) |
| C(5) | −0.125(1) | 0.3168(6) | 0.5778(6) | 8.1(3) |
| C(6) | −0.137(1) | 0.2457(7) | 0.5799(5) | 7.7(3) |
| C(7) | −0.104(1) | 0.2053(5) | 0.5174(5) | 6.1(2) |
| C(8) | 0.1178(7) | 0.0513(4) | 0.1617(4) | 3.4(2) |
| C(9) | 0.1571(7) | 0.0117(4) | 0.0921(4) | 3.5(2) |
| C(10) | 0.1438(9) | 0.0412(4) | 0.0178(5) | 5.1(2) |
| C(11) | 0.178(1) | 0.0034(6) | −0.0450(5) | 6.5(3) |
| C(12) | 0.223(1) | −0.0643(5) | −0.0334(5) | 6.6(2) |
| C(13) | 0.234(1) | −0.0927(5) | 0.0395(6) | 6.3(2) |
| C(14) | 0.2008(8) | −0.0554(4) | 0.1030(5) | 4.7(2) |
| C(15) | 0.2521(7) | 0.1876(4) | 0.2911(4) | 3.6(2) |
| C(16) | 0.3779(7) | 0.2227(4) | 0.3037(4) | 3.9(2) |
| C(17) | 0.4851(8) | 0.1881(5) | 0.3335(5) | 5.2(2) |
| C(18) | 0.5999(9) | 0.2198(6) | 0.3447(6) | 6.5(3) |
| C(19) | 0.6070(9) | 0.2899(6) | 0.3281(6) | 6.4(2) |
| C(20) | 0.504(1) | 0.3263(5) | 0.3004(6) | 6.6(3) |
| C(21) | 0.3860(9) | 0.2932(5) | 0.2867(5) | 5.4(2) |
| C(22) | −0.1544(7) | 0.0467(4) | 0.2663(4) | 3.4(2) |
| C(23) | −0.2764(7) | 0.0090(4) | 0.2530(4) | 3.3(2) |
| C(24) | −0.2834(8) | −0.0614(4) | 0.2739(5) | 4.6(2) |
| C(25) | −0.3941(9) | −0.0967(5) | 0.2599(6) | 5.8(2) |
| C(26) | −0.4990(9) | −0.0651(5) | 0.2261(6) | 6.1(2) |
| C(27) | −0.4933(9) | 0.0048(5) | 0.2048(7) | 6.8(3) |
| C(28) | −0.3822(8) | 0.0406(5) | 0.2185(5) | 5.1(2) |
| S(1) | −0.1943(4) | 0.2997(2) | 0.0154(2) | 9.00(9) |
| C(29) | −0.287(1) | 0.2849(7) | 0.0891(8) | 8.9(4) |
| C(30) | −0.226(1) | 0.2486(5) | 0.1438(6) | 7.3(3) |

*(continued)*

***Table IV.*** Continued

| Atom | x | y | z | B(Å$^2$) |
|---|---|---|---|---|
| C(31) | −0.0760(9) | 0.2546(5) | 0.0714(5) | 5.5(2) |
| N(1) | 0.033(1) | 0.2450(5) | 0.0474(6) | 10.3(3) |
| S(2) | 0.3209(4) | −0.0455(2) | 0.5384(2) | 9.49(9) |
| C(32) | 0.293(1) | −0.0363(6) | 0.3925(6) | 8.4(3) |
| C(33) | 0.367(1) | −0.0668(7) | 0.4510(8) | 10.0(4) |
| N(4) | 0.1958(7) | 0.0019(3) | 0.4133(4) | 4.3(2) |
| C(34) | 0.2010(9) | 0.0013(5) | 0.4889(5) | 5.4(2) |
| N(3) | 0.121(1) | 0.0384(5) | 0.5305(5) | 7.9(3) |
| H(01) | 0.0975 | 0.2194 | 0.0786 | 5* |
| H(02) | 0.0477 | 0.2624 | −0.0027 | 5* |
| H(03) | 0.0540 | 0.0668 | 0.5045 | 5* |
| H(04) | 0.1350 | 0.0404 | 0.5871 | 5* |
| H(6) | −0.1716 | 0.2222 | 0.6252 | 5* |
| H(7) | −0.1081 | 0.1536 | 0.5193 | 5* |
| H(10) | 0.1093 | 0.0887 | 0.0107 | 5* |
| H(11) | 0.1723 | 0.0258 | −0.0976 | 5* |
| H(12) | 0.2446 | −0.0928 | −0.0773 | 5* |
| H(13) | 0.2687 | −0.1397 | 0.0480 | 5* |
| H(14) | 0.2068 | −0.0768 | 0.1552 | 5* |
| H(17) | 0.4786 | 0.1390 | 0.3475 | 5* |
| H(18) | 0.6760 | 0.1934 | 0.3644 | 5* |
| H(19) | 0.6880 | 0.3138 | 0.3363 | 5* |
| H(20) | 0.5108 | 0.3764 | 0.2882 | 5* |
| H(21) | 0.3103 | 0.3200 | 0.2651 | 5* |
| H(24) | −0.2082 | −0.0858 | 0.2984 | 5* |
| H(25) | −0.3975 | −0.1461 | 0.2741 | 5* |
| H(26) | −0.5779 | −0.0909 | 0.2159 | 5* |
| H(27) | −0.5692 | 0.0286 | 0.1809 | 5* |
| H(28) | −0.3780 | 0.0896 | 0.2016 | 5* |
| H(29) | −0.3745 | 0.3020 | 0.0893 | 5* |
| H(30) | −0.2669 | 0.2313 | 0.1891 | 5* |
| H(32) | −0.4399 | −0.0963 | 0.4424 | 5* |
| H(33) | −0.3046 | −0.0402 | 0.3380 | 5* |
| H(3) | −0.0369 | 0.3305 | 0.4003 | 5* |
| H(4) | −0.0802 | 0.3980 | 0.5175 | 5* |
| H(5) | −0.1440 | 0.3438 | 0.6217 | 5* |

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2\,B(1,1)+b^2\,B(2,2)+c^2\,B(3,3)+ab\cos\gamma B(1,2)+ac\cos\beta\,B(1,3)+bc\cos\alpha B(2,3)]$.

Therefore, the oxidative addition reaction is an easy and available method for the synthesis of binuclear copper(II) complexes.

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Referee I: R. D. Pike
Referee II: D. Rabinovich