

双核铜(II)配合物的合成——氧化加成反应

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Synthesis of Binuclear Copper (II) Complex — Oxidative Addition Reaction

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At room temperature, dibenzoyl peroxide undergoes oxidative addition reaction with metallic copper powder and 4-dimethylamine-pyridine which affords the last products as binuclear copper (II) complex (1), $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_7\text{H}_{10}\text{N}_2)]_2$. This complex is further characterized by spectroscopic methods. The structure of complex (1) has been determined by a single-crystal X-ray analysis. Crystallographic data are as follows: monoclinic, space group $P2_1/n$, $a = 10.446(2)\text{Å}$, $b = 11.140(5)\text{Å}$, $c = 17.179(3)\text{Å}$, $\beta = 95.92(3)^\circ$, $V = 1988.4(7)\text{Å}^3$, $Z = 4$, $F(000) = 884$, $\mu = 11.27\text{cm}^{-1}$, $D(\text{calcd.}) = 1.429\text{g}\cdot\text{cm}^{-3}$, $R = 0.0399$, $R_w = 0.1202$. Each copper (II) ion is coordinated by two bridging bidentate benzoate and 4-dimethylamine-pyridine to form dimeric molecule. CCDC: 188744.

Keywords: copper complex oxidative addition magnetic property

0 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. Copper (II) complexes are widely used as catalysts in the decomposition of disubstituted peroxides^[1,2]. To obtain insight into the correlation between the structure and nature of copper catalysts, low-molecular-weight coordination compounds may be prepared. 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 bin-

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uclear 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 binuclear compounds of transition metals constitutes a field of continuing research interest, this report concerns an oxidative preparation method of the copper (II) complexes. In this work we have prepared binuclear copper (II) compound by oxidative addition reaction. X-ray structure analysis of the prepared binuclear copper (II) complex $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_7\text{H}_{10}\text{N}_2)]_2$ is reported. It also describes a detailed study of spectroscopic properties of the title compound.

1 Experimental

1.1 Preparation

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification for the preparation of the complex. Elemental analyses were performed on an ERBA-1106 instrument (Italy). Copper was determined using a JA96-975 ICP-AES (Inductively Coupled Plasmas Atomic Emission Spectrometer). Molecular weight determinations were made on chloroform solutions at 25° using CORONA-117 analyser (American instrument). IR spectrum was recorded on a Nicolet 170SX IR spectrophotometer in Nujol on CsI. Electronic spectra were observed with a Hitachi 330 spectrophotometer. Magnetic measurements were carried out with a polycrystalline sample on a pendulum type magnetometer equipped with a nitrogen continuous-flow cryostat working in the 77 ~ 300K range.

4-Dimethylamine-pyridine (1mmol, 122mg) was added to a mixture of dibenzoyl peroxide (1mmol, 242mg) and copper powder(1mmol, 63.5mg) in a mixed solvent of methanol (30mL) and acetone (30mL). The mixture was stirred for 24h at room temperature. The resulting green solution was filtered and left to yield green crystals (1). Yield: 66%. Anal. calcd. For $\text{C}_{42}\text{H}_{40}\text{Cu}_2\text{N}_4\text{O}_8$, C: 58.94; H: 4.71; N: 6.55; Cu: 14.8%. Found C: 58.69; H: 4.61; N:

6.36; Cu: 14.6%.

1.2 Crystal Structure Determination

A green prismatic crystal of the complex (1) of dimensions was selected and mounted on an automatic Enraf-Nonius CAD-4 four-circle diffractometer^[3]. Intensities were collected with a graphite monochromator and Mo $K\alpha$ radiation ($\lambda = 0.71073\text{\AA}$). All non-hydrogen atoms were refined by the full-matrix least-squares with anisotropic temperature factors. Hydrogen atoms were located from the difference Fourier map and refined isotropically. Computations were performed using SDP program on a PDP11/44 computer. Crystal data and structure refinement are listed in Table 1.

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Table 1 Crystal Data and Structure Refinement

chemical formula	$\text{C}_{42}\text{H}_{40}\text{Cu}_2\text{N}_4\text{O}_8$
crystal size / mm^3	$0.5 \times 0.4 \times 0.3$
formula weight	855.9
temperature / K	293(2)
crystal system	monoclinic
space group	$P2_1/n$
$a / \text{\AA}$	10.446(2)
$b / \text{\AA}$	11.140(5)
$c / \text{\AA}$	17.179(3)
$\beta / (^\circ)$	95.92(3)
volume / \AA^3	1988.4(7)
Z	4
density (calculated) / ($\text{Mg} \cdot \text{m}^{-3}$)	1.429
absorption coefficient / mm^{-1}	1.127
$F(000)$	884
θ range for data collection	$2.18^\circ < \theta < 24.96^\circ$
limiting indices	$0 \leq h \leq 12, 0 \leq k \leq 13,$ $-20 \leq l \leq 20$
reflections collected	3702
independent reflections	3496 ($R_m = 0.0278$)
absorption correction	PSI
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	3496/0/253
goodness-of-fit on F^2	1.093
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0399, wR_2 = 0.1202$
R indices (all data)	$R_1 = 0.0551, wR_2 = 0.1421$
largest diff. peak and hole / ($e \cdot \text{\AA}^{-3}$)	0.828 and -0.482

2 Results and Discussion

2.1 Synthesis

Dibenzoyl peroxide and 4-dimethylamine-pyridine reacted with metallic copper powder at room temperature giving green solution, the copper powder is ob-

served to dissolve rapidly. After a few days, green crystals were deposited in good yield. This indicates the formation of copper (II) compound. The mechanism of the oxidative addition reaction is probably stepwise as the benzoyl radical reacts with copper to give copper (I) benzoate which then in a subsequent reaction with a further benzoyl radical result 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 color changes in the procedure of the title complex synthesis and obtained results, metallic copper powder has been oxidized to form Cu (II) complex. Therefore, direct use of metallic copper powder is characteristic of the present synthetic method. Molecular weight was measured in CHCl_3 solution (Found: 853.1, calcd.: 855.9). The compound was soluble enough for measurements. Results are quite reproducible and seem to be scarcely influenced by concentration in the accessible range. In the case of present complex, molecular-weight measurements give values strongly suggesting the existence of expected binuclear species. The complex is stable in air at room temperature. It is easily soluble in acetone and methanol, and sparingly soluble in benzene and hexane. Therefore, the binuclear Cu (II) complex with coordinated benzoate group can be obtained with high yields through oxidative addition reaction. The elemental analysis of the title complex agreed well with its formula.

2.2 Spectroscopic Characterization

Benzoate may coordinate to a metal ion in one of the following modes: uni-dentate, bidentate and bridging. IR data shows the existence of the bridging benzoate through the observation of characteristic absorption bands ($1600 \sim 1400$, $950 \sim 710$, $500 \sim 600 \text{ cm}^{-1}$)^[4]. IR of the title complex is consistent with other known bridged carboxylate metal complexes as determined by the position and separation between the antisymmetric (ν_{as}) and symmetric (ν_s) stretches of the carboxylate^[5,6]. The title complex exhibits carboxylate stretches at 1621 and 1404 cm^{-1} , respectively, where $\Delta\nu(\nu_{asym} - \nu_{sym})$ is 217 cm^{-1} , consistent with a bridging

mode^[5]. In the range $950 \sim 700$ and $500 \sim 600 \text{ cm}^{-1}$, there disappear the characteristic absorption bands of $\delta_{(\text{COO})}$ and $\pi_{(\text{COO})}$, respectively. These are the characteristics of the typical bridging coordination benzoate^[7,8]. They are consistent with the results of crystal structure analysis of copper (II) complex $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_7\text{H}_{10}\text{N}_2)]_2$.

The observed absorption band maximum in the electronic spectra, as well as the IR spectra, agreed with those in the literature^[9]. The wide bands (676 nm) belongs to $d-d$ transitions of the copper (II), while shoulder band (370 nm) is characteristic of the bridging system with antiferromagnetic interaction^[9].

2.3 Magnetic Property of the Complex

The title binuclear copper (II) complex is paramagnetic at room temperature for single copper showing an antiferromagnetic interaction, which is usually found for this type copper (II) compounds. Magnetic measurements of the crystalline complexes have been studied over the temperature range $77 \sim 300 \text{ K}$. From the isotropic spin hamiltonian $H = -2JS_1 \cdot S_2$, where $S_1 = S_2 = 1/2$, the expression of χ_m is

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

where N , β , k and g have the usual meaning, $N_\alpha = 1.50 \times 10^{-9} \text{ m}^2 \cdot \text{mol}^{-1}$. J is the exchange integral, $J > 0$, there is ferromagnetic interaction between magnetic metal ions, $J < 0$, there is antiferromagnetic interaction between magnetic metal ions. Least-squares fitting of experimental magnetic data with the above equation gave the superexchange parameters, $g = 2.03$, $-2J = 301.1 \text{ cm}^{-1}$, $F = 2.3 \times 10^{-6}$, where F is the quality factor defined as $F = \sum (\chi_o - \chi_c)^2 / \chi_o$. It is characteristic of spin-coupled copper (II) complexes

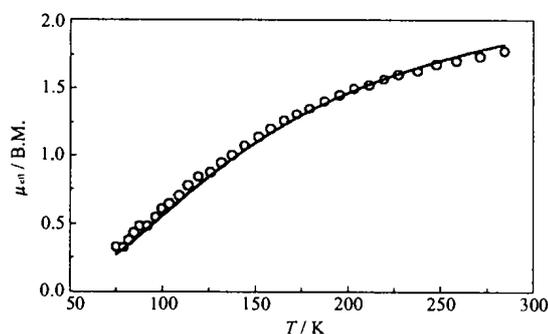


Fig. 1 Experimental μ_{eff} vs temperature for the title compound

with a single ground state. The value of the superexchange parameter for the title compound should be considered as normal, taking into account the structural and magnetic data found in the literature for binuclear copper (II) complexes^[7-9].

2.4 Crystal Structure

Selected bond distances and angles of the complex (1) are listed in Table 2. Fig. 2 illustrates the conformation of the molecule. There have been many structural reports concerning bridged binuclear copper (II) compounds^[7-9], similar to the present complex. The carboxylate bridged Cu...Cu distance of the present compound is found to be 2.6980(9) Å, which is comparable to that in tetrakis(benzoate)-bis(triphenylphosphine oxide) dicopper (II), 2.657(1) Å^[8].

The five coordinate atoms arrange a distorted square pyramid with N atom from 4-dimethylamine-

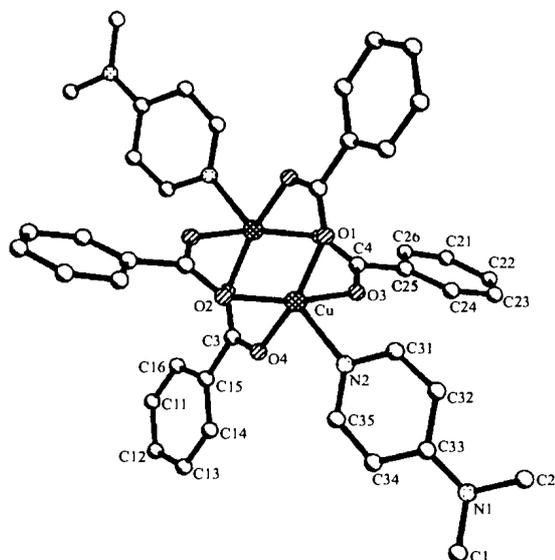


Fig. 2 Molecular structure of $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_7\text{H}_{10}\text{N}_2)]_2$

pyridine at the apical position. The C-O distances in the complex are not significantly different (av. 1.252 Å), and possess comparable values to those in other benzoate-bridging dicopper complex^[6]. All other bond distances and angles are within normal ranges. In the binuclear copper (II) complex $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_7\text{H}_{10}\text{N}_2)]_2$, the Cu atom is coordinated by five atoms: four oxygen atoms belong to bridging carboxyl groups, and one N atom to 4-dimethylamine-pyridine. Two benzoate groups and two ligands 4-dimethylamine-pyridine are respectively located on the opposite sides to minimize repulsion between the ligands.

The complex (1) has the expected dimeric form which is bridged via the copper atoms with the carboxylate groups. The coordination around the copper (II) ion is distorted square-pyramidal. Four oxygen atoms lie in the basal plane with interatomic distances of Cu-O [av. 1.977(3) Å], and similar values have been observed in tetrakis(benzoate) bis(triphenylphosphine oxide) dicopper (II) (av. 1.968 Å)^[8]. The nearest neighbours of the copper atom are the four oxygen atoms of the bridging benzoate ligands. A distorted square-based pyramidal arrangement about the copper atom is completed by the nitrogen of 4-dimethylamine-pyridine ligand at 2.144(3) Å from the copper atom. The eight-membered ring of Cu O(1) C(3A) O(4A) Cu(A) O(1A) C(3) O(4) and Cu O(3) C(4) O(2A) Cu(A) O(3A) C(4A) O(2) are in the basal plane conformation. The dihedral angle is 86.9°.

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

Table 2 Selected Bond Lengths(Å) and Angles(°)

Cu-O(1)	1.969(3)	Cu-O(2)	1.977(3)	Cu-O(3)	1.980(3)
Cu-O(4)	1.981(3)	Cu-N(2)	2.144(3)	Cu-Cu(A)	2.6980(9)
O(4)-C(3)	1.257(4)	O(3)-C(4)	1.248(4)		
O(1)-Cu-O(2)	89.26(12)	O(1)-Cu-O(3)	88.23(12)	O(2)-Cu-O(3)	166.13(11)
O(1)-Cu-O(4)	166.24(11)	O(2)-Cu-O(4)	88.93(12)	O(3)-Cu-O(4)	90.28(12)
O(1)-Cu-N(2)	97.95(11)	O(2)-Cu-N(2)	103.59(11)	O(3)-Cu-N(2)	90.27(11)
O(4)-Cu-N(2)	95.74(11)	O(1)-Cu-Cu(A)	84.12(8)	O(2)-Cu-Cu(A)	87.74(8)
O(3)-Cu-Cu(A)	78.44(8)	O(4)-Cu-Cu(A)	82.17(8)	N(2)-Cu-Cu(A)	168.47(9)
C(3)-O(4)-Cu(A)	125.1(2)				

Symmetry transformations used to generate equivalent atoms: $-x, -y, -z$.

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全国地球化学分析学术报告会 X 射线光谱分析研讨会 征文通知

为促进我国分析技术,特别是地球化学分析技术的学术交流,增进分析化学家们的互相了解,推动分析测试技术的进步,中国地质学会拟于 2003 年 5 月在北京召开全国地球化学分析学术报告会和 X 射线光谱分析研讨会。

会议将重点邀请国内外知名专家和学者,对分析科学及相关领域的研究进展进行评述,报告最新研究成果。同时亦热忱欢迎广大分析工作者和专家投稿,参会并交流经验。对有价值的论文,将由《岩矿测试》杂志择优发表。

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(1) 各种分析测试技术的进展与评述; (2) 地质样品中的主、次、痕量元素分析方法研究; (3) 同位素地球化学研究; (4) 有机与形态地球化学分析; (5) 环境地球化学分析; (6) 大陆科学钻探与现场分析技术; (7) 信息与计算机技术。

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(1) X 射线探测技术的最新发展、原理与应用; (2) 偏振 X 射线荧光分析技术; (3) 常规能量色散 XRF 技术的现状、应用与局限; (4) 小型与原位 X 射线荧光分析仪研制进展; (5) 微束 X 射线荧光分析技术; (6) 基体校正与化学计量学研究现状; (7) 样品制备技术; (8) XRF 应用: 文物考古、生物医学、环境等。

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