

利用氧化加成反应合成双核铜(II)配合物及其性质

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室温下, 在 2, 4, 6- 三甲基吡啶存在下, 利用过氧化苯甲酰和金属铜粉的氧化加成反应制备了双核铜(II)配合物 $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_8\text{H}_{11}\text{N})]_2$ (**1**), 研究了配合物的物理化学和光谱学性质, 配合物属单斜晶系, 空间群为 $P2_1/n$, $a = 10.499(4) \text{ \AA}$, $b = 10.666(6) \text{ \AA}$, $c = 18.109(3) \text{ \AA}$, $\beta = 92.92(2)^\circ$, $V = 2025.2 \text{ \AA}^3$, $Z = 2$, $D_c = 1.398 \text{ g} \cdot \text{cm}^{-3}$, $R = 0.0676$, $R_w = 0.0749$ 。中心铜离子由桥式双齿苯甲酸根和 2, 4, 6- 三甲基吡啶配位形成二聚双核配合物。

关键词: 铜 双核配合物 氧化加成

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Synthesis and Properties 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 the ligand (2, 4, 6-trimethylpyridine) which affords the last products as binuclear copper (II) complex (**1**), $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_8\text{H}_{11}\text{N})]_2$. This complex is further characterized by physico-chemical and spectroscopic methods. Crystals (**1**) are monoclinic, space group $P2_1/n$, $a = 10.499(4) \text{ \AA}$, $b = 10.666(6) \text{ \AA}$, $c = 18.109(3) \text{ \AA}$, $\beta = 92.92(2)^\circ$, $V = 2025.2 \text{ \AA}^3$, $D_c = 1.398 \text{ g} \cdot \text{cm}^{-3}$, $Z = 2$, $R = 0.0676$, $R_w = 0.0749$. Each copper^{II} ion is coordinated by two bridging bidentate benzoate and 2, 4, 6-trimethylpyridine to form dimeric binuclear molecule.

Keywords: copper binuclear complex oxidative addition

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]. Ox-

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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, 2]. To obtain insight into the correlation between the structure and nature of copper catalysts, low-molecular-weight coordination compounds may be prepared. 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 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 $[\text{Cu}(\text{C}_8\text{H}_{11}\text{N})(\text{C}_6\text{H}_5\text{COO})_2]_2$ is reported. It also describes a detailed study of spectroscopic properties of the title compound.

1 Experimental

1.1 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 (Italy). Copper was determined using JA96-970 spectrometer. Molecular weight determinations were made on chloroform solutions at 25° using CORONA-117 analyser (American instrument). IR spectra was recorded on a Nicolet 170SX IR spectrophotometer in Nujol on CsI. TG was carried out under N₂ purge, heating at 5°C · min⁻¹ on a PE-TGS-2 thermal analyzer. Conductivity measurements were carried out in thermostatic bath of acetone solution at 25° using DDS-11A analyser. Electronic spectrum was 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 75 ~ 300 K range. MCD spectra was recorded on JASCD-J20C automatic spectropolarimeter (magnetic field: 7000 Gauss, pool length: 0.5cm, scale: 0.002° · cm⁻¹). Cyclic voltammogram was obtained in CH₂Cl₂ (0.1 mol · L⁻¹ Bu₄NClO₄) using an MEC-12A analyzer and a conventional three-electrode system at 25°C. The platinum working electrode was in the form of a disc and used in a stationary mode, the auxiliary electrode was a platinum plate with an area of 2 × 8 mm², and the reference electrode was a saturated calomel electrode (SEC).

1.2 Synthesis of the complex

2, 4, 6-Trimethylpyridine (1mmol, 121mg) was added to a mixture of dibenzoyl peroxide (1 mmol, 242 mg) and copper powder (1 mmol, 63.5 mg) in a mixed solvent of methanol (30 mL) and THF (30 mL). The mixture was stirred for 48h at room temperature. The resulting green solution was filtered and left to yield green crystals (1). Yield: 71%. Anal. calcd. for C₄₄H₄₂Cu₂N₂O₈: C: 61.90; H: 4.92; N: 3.28; Cu: 14.9%. Found C: 61.79; H: 4.81; N: 3.11; Cu: 14.7%.

1.3 X-ray data collection^[3]

A green prismatic crystal of the complex (1) of dimensions (0.10 × 0.15 × 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 Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), using the ω -2 θ scan technique. Three thousand nine hundred and eighty-five independent reflections were collected in the range of $1^\circ < \theta < 25^\circ$, 1867 of which were assumed as observed [$I \geq 3\sigma(I)$]. Lorentz, polarization and absorption corrections were applied to the intensity data. The structure was solved by direct methods and Fourier synthesis. 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 the SDP program on a PDP11/44 computer. Crystallographic data are as follows: monoclinic, space group $P2_1/n$, $a = 10.499(4) \text{ \AA}$, $b = 10.666(6) \text{ \AA}$, $c = 18.109(3) \text{ \AA}$, $\beta = 92.92(2)^\circ$, $V = 2025.2 \text{ \AA}^3$, $Z = 2$, $D_c = 1.398 \text{ g} \cdot \text{cm}^{-3}$, $R = 0.0676$, $R_w = 0.0749$.

2 Results and discussion

2.1 Preparation of the complex

Dibenzoyl peroxide and 2, 4, 6-trimethylpyridine reacted with metallic copper powder at room temperature giving green solution, the insoluble copper powder is observed 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 Cu 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 colour changes in the procedure of the title complex synthesis and obtained results, metallic copper powder has been oxidated 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. 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. Its molar conductivity in acetone shows that it is non-electrolyte and existed as a molecule. Therefore, the binuclear Cu (II) complexes with coordinated benzoate group can be obtained with high yield through oxidative addition reaction. The elemental analysis of the title complex agreed well with its formula.

The electrochemical property of complex (1) was investigated by cyclic voltammetry. Complex (1) showed a quasi-reversible wave at $E_{pa} = -0.05 \text{ V}$, $E_{pc} = -0.35 \text{ V}$ in CH_2Cl_2 at scan rate $100 \text{ mV} \cdot \text{s}^{-1}$.

2.3 IR

Benzoate may coordinate to a metal ion in one of the following modes: unidentate, bidentate and bridging. IR data shows the existence of the bridging benzoate through the observation of charac-

teristic absorption bands ($1600 \sim 1400$, $950 \sim 700$, $500 \sim 600\text{cm}^{-1}$)^[4]. IR of the title complex are 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 1576 and 1400cm^{-1} , respectively, where $\Delta\nu(\nu_{\text{asym}} - \nu_{\text{sym}})$ is 176cm^{-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. The band of $\nu_{\text{C=O}}$ at 1720cm^{-1} is absent in the IR spectrum of complex (1). These are the characteristics of the typical bridging coordination benzoate^[7,8]. They are consistent with the results of crystal structure of the copper (II) complex $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_8\text{H}_{11}\text{N})]_2$.

The observed absorption band maxima in the electronic spectra, as well as the IR spectra, agreed with those in the literature^[9]. The broad bands (687nm) belongs to $d-d$ transitions of the copper (II), while shoulder band (324nm) is characteristic of the bridging system with antiferromagnetic interaction^[9].

2.4 Thermal analysis of complexes

The TG-DTA thermogram of the complex (1) reveals that the pyrolytic decomposition takes place in two steps. The first one corresponds to a weight loss of 26.6% and is probably due to decomposition of the ligand 2, 4, 6-trimethyl-pyridine (loss of weight calculated 28.4%). The decomposition process is confirmed by a strong endothermic peak at $196 \sim 316^\circ\text{C}$. The second step corresponds to, in the $316 \sim 650^\circ\text{C}$ temperature range, 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. 18.6%).

2.5 Magnetic property of the complexes

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 $75 \sim 300\text{K}$. From the isotropic spin Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$, where $S_1 = S_2 = 1/2$, the expression of χ_{m} is

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

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 the experimental magnetic data with the above equation gave the magnetic parameters, $g = 2.02$, $-2J = 208.1\text{cm}^{-1}$, $F = 3.0 \times 10^{-6}$, where F is the quality factor defined as $F = \sum (\chi_0 - \chi_c)^2 / \chi_0$. It is characteristic of spin-coupled copper (II) complexes 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 ($J = -143.4\text{cm}^{-1}$) found for binuclear copper (II) complex $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})(\text{C}_6\text{H}_5\text{COO})_2]_2$ ^[7]. Compared with magnetic data ($J = -434\text{cm}^{-1}$) of $[\text{Cu}_2(\text{HCOO})_4(\text{DMSO})_2]$, the substitution of a R group for the hydrogen in $[\text{Cu}_2(\text{RCOO})_4\text{L}_2]$ dimers leads to a significant weakening of the coupling between copper ions^[8]. Hoffman and coworkers applied a

molecular-orbital treatment focusing on the effect of the electron-withdrawing properties of the R group on the copper (II)-copper (II) interactions^[9]. In fact, some outstanding parameters involving the metal atoms such as the Cu-Cu or the Cu-O distances and the C-O-Cu angle are not correlated with the copper (II)-copper (II) interaction.

2.6 Magnetic circular dispersion spectrum(MCD)

In general, the interaction between monocolour circular light and substance may be described by two absorption coefficient. The difference between two absorption coefficient is circular dispersion spectra. The magnetic interactions between antiferromagnetic substance may be explored through Faraday parameter of magnetic circular dispersion spectrum. Experimental data: (1), $5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (acetone solution), $\lambda_{\text{max}} = 510, 290 \text{ nm}$, $[\theta]_{\text{M}} = -7.26 \times 10^{-2}, +4.82 \times 10^{-2}$, $B = +5.10 \times 10^{-5}, -3.86 \times 10^{-4}$, $[\theta]_{\text{M}}$: ovality/Gauss $\cdot \text{mol}$. Faraday parameter(B) was calculated from

$$\int_0^{\infty} ([\theta]_{\text{M}} / \nu) d\nu = -33.5294 (B + C/kT)$$

MCD data of the complex $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_8\text{H}_{11}\text{N})]_2$ show positive peak at 290 nm in UV region and negative peak at 510 nm in visible region. The former is attributed to $A_{1g} \rightarrow {}^1B_{2u}$ transition of benzenoid structure. There are positive clock-form curve in Faraday (B) drawing because of blending of ${}^1B_{2u}$ and ${}^1B_{1u}$ energy level. The negative MCD peaks(510nm) result from $d_{xy} \rightarrow d_{x^2-y^2}$ transitions. The blending of 3 d and 4 p orbital gives rise to non-zero rotation strength with magnetic field. MCD of the complex only bring about Faraday parameter(B), Faraday parameter(A) are absent. Faraday parameter(A) is related to magnetic moment. The absence of (A) showed anti-ferromagnetic interaction between copper atoms. This results coincide with magnetic determination data, and confirm the formation of binuclear complex.

2.7 Crystal structure

Selected bond distances and angles of the complex(1) are listed in Table 1. Fig. 1 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 2.661(4) Å, which is comparable to that in tetrakis (benzoate)-bis(triphenylphosphine oxide) dicopper (II), 2.657(1) Å^[10].

Table 1 Selected Bond Lengths(Å) and Angles(°) for the Complex (1)

bond distances			
Cu-Cu'	2.661(4)	Cu-O(1)	1.973(7)
Cu-O(3)	1.975(7)	Cu-N	2.155(10)
C(1)-O(1)	1.272(12)	C(1)-O(2)	1.228(13)
C(2)-O(3)	1.259(13)	C(2)-O(4)	1.252(13)
bond angles			
O(1)-Cu-O(3)	89.1(3)	O(1)-Cu-N	99.4(3)
O(3)-Cu-N	97.8(4)	Cu-O(1)-C(1)	122.6(7)
Cu-O(3)-C(2)	123.6(7)	Cu-N-C(31)	117.0(1)
Cu-N-C(35)	118.0(1)	O(1)-C(1)-O(2)	124.0(1)

The five coordinate atoms form a distorted square-pyramid with N atom from 2, 4,

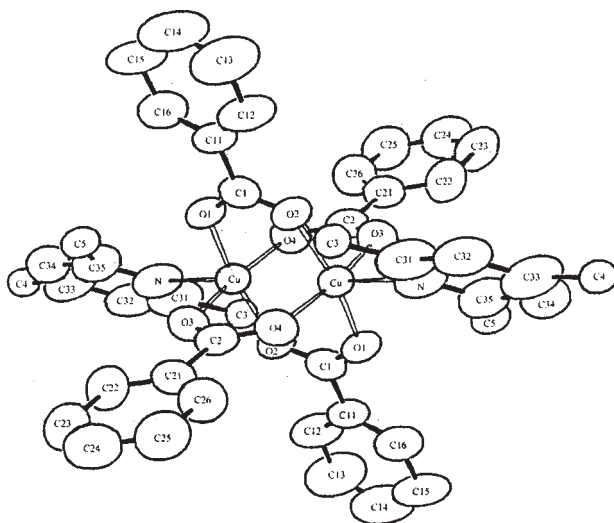


Fig. 1 Molecular structure of $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_8\text{H}_{11}\text{N})]_2$

6-trimethylpyridine at the apical position. The C-O distances in the complex are not significantly different (av. 1.253\AA), and possess comparable values to those in other benzoate-bridging dicopper complex^[6]. All other bond distances and angles are within normal ranges^[11, 12].

In the binuclear copper (II) complex $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{C}_8\text{H}_{11}\text{N})]_2$, the Cu atom is coordinated by five atoms: four oxygens belong to bridging carboxy groups, and one N atom to 2, 4, 6-trimethylpyridine. Two benzoate groups and two ligands 2, 4, 6-trimethylpyridine are respectively located on the opposite sides to minimise repulsion between the ligands.

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. $1.974(7)\text{\AA}$], and similar values have been observed in tetrakis(benzoate) bis(triphenylphosphine oxide) dicopper (II) (av. 1.968\AA)^[10]. 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 2, 4, 6-trimethylpyridine ligand at $2.155(10)\text{\AA}$ from the copper atom. The eight-membered ring of Cu O(1) C(1) O(2) Cu'O(1') C(1') O(2') and Cu O(3) C(2) O(4) Cu' O(3') C(2') O(4') are in the basal plane conformation. The dihedral angle is 88.7° . Therefore, oxidative addition reaction is feasible for the synthesis of binuclear copper (II) complexes.

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