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双核铜配合物的合成与晶体结构

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室温下, 在吡啶-2-甲酸存在下, 过氧化苯甲酰和金属铜粉经过氧化加成反应生成双核铜(II)配合物, $[\text{Cu}(\text{C}_6\text{H}_5\text{NO}_2)(\text{C}_6\text{H}_5\text{COO})_2]_2$, X-射线单晶结构分析确定了配合物的分子和晶体结构. 晶体属单斜晶系, 空间群为 $P2_1/a$, 晶胞参数如下: $a=10.423(5) \text{ \AA}$, $b=10.511(3) \text{ \AA}$, $c=16.896(11) \text{ \AA}$, $\beta=99.37(5)^\circ$, $V=1826.4 \text{ \AA}^3$. 中心铜离子由桥式双齿苯甲酸根和吡啶-2-甲酸配位形成二聚双核配合物, 同时通过红外光谱和热分析表征了配合物的性质.

关键词: 铜 双核配合物 氧化加成
分类号: O611.622

双核铜 晶体结构

SYNTHESIS AND CRYSTAL STRUCTURE OF BINUCLEAR COPPER(II) COMPLEX

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At room temperature, dibenzoyl peroxide undergoes oxidative addition reaction with metallic copper powder and 2-picolinic acid which afford the last product as binuclear copper(II) complexes, $[\text{Cu}(\text{C}_6\text{H}_5\text{NO}_2)(\text{C}_6\text{H}_5\text{COO})_2]_2$. The crystal and molecular structure of the title complex has been determined by single crystal X-ray analysis. Crystals(1) are monoclinic, the space group is $P2_1/a$, $a=10.423(5) \text{ \AA}$, $b=10.511(3) \text{ \AA}$, $c=16.896(11) \text{ \AA}$, $\beta=99.37(5)^\circ$, $V=1826.4 \text{ \AA}^3$. Each copper(II) ion is coordinated by bridging bidentate benzoate ligands and 2-picolinic acid to form dimeric binuclear molecules. The structure of the compound(1) shows a clear centre of symmetry. The complex is further characterized by its IR and thermal properties.

Keywords: copper binuclear complex oxidative addition

0 Introduction

Binuclear copper complexes are very important in coordination chemistry and catalytic reactions.

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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^[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 binuclear copper(II) complexes which would possess novel coordination chemistry. Generally, the Cu(II) complexes are obtained by reacting Cu(I) salts and ligands. Since the investigation of dinuclear compounds of transition metals constitutes a field of continuing research interest, we report here a novel method of preparing copper complexes which depends on the oxidative-addition reaction of the O-O bond in dibenzoyl peroxide on metallic copper powder. In this work we first prepared the binuclear copper(II) compounds $[\text{Cu}(\text{C}_6\text{H}_5\text{NO}_2)(\text{C}_6\text{H}_5\text{COO})_2]_2$ by the oxidative addition reaction. The X-ray structure analysis of the prepared binuclear copper(II) complex $[\text{Cu}(\text{C}_6\text{H}_5\text{NO}_2)(\text{C}_6\text{H}_5\text{COO})_2]_2$ are reported. It also describes a detailed study of the spectroscopic properties of the title compounds.

1 Experimental

1.1 Physical measurements

Commercially available purest samples of various chemicals were used for the preparation of the complexes.

Elemental analyses were performed on an ERBA-1106 instrument (Italy). Copper was determined using a 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 N_2 purge, 25 mL \cdot min⁻¹, heating at 5° \cdot min⁻¹, on a PE-TGS-2 instrument thermal analyzer. Conductivity measurements were carried out on acetone solutions thermostatted at 25° using DDS-11A analyser. Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Electronic spectra was observed with a Hitachi 330 spectrophotometer.

1.2 Synthesis of the complex

2-Picolinic acid (1 mmol, 123 mg) 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 (20 mL) and acetone (20 mL). The solution was stirred for 48 h at room temperature. The resulting blue solution was filtered and left to yield blue crystals. They were washed and dried in vacuo. Yield; 69%. Found C=56.21, H=3.39, N=3.36, Cu=14.2, $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_{12}\text{Cu}_2$ requires C=56.00, H=3.50, N=3.27, Cu=14.8%. m. p. = 240°C (decompose). The measured molecular weight is 859 (calcd. 857.75).

Therefore, direct use of metallic copper powder and dibenzoyl peroxide is characteristic of the pre-

sent novel synthetic method which is significantity different from previous preparation of the binuclear copper(II) complexes (direct use of copper(II) salts and ligands).

The complexes are stable in air at room temperature. It is easily soluble in THF, acetone and methanol, and sparingly soluble in benzene and hexane. Their molar conductivity ($4.5 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) in acetone shows that they are nonelectrolyte and existed as a molecular^[3].

1.3 X-ray data collection

A blue single crystal of the title compound with dimensions of $0.54 \times 0.36 \times 0.45 \text{ mm}$ was selected and mounted on the tip of a glass fiber with epoxy resin for X-ray diffraction studies. The determination of the unit cell and the data collection were performed with graphite-monochromatized MoK α radiation ($\lambda = 0.071073 \text{ nm}$) on an Enraf Nonius CAD4 diffractometer. A total of 3596 independent reflections were collected in the range of $1^\circ < \theta < 25^\circ$ by ω - 2θ scan technique at room temperature, in which 1742 reflections with $I \geq 3\sigma(I)$ were considered to be observed and used in the succeeding refinements. The unit-cell parameters were obtained by least-squares refinement of the setting angles for 25 reflections. No significant change was detected in the intensity of the three standard reflections. Lorentz, polarization and absorption corrections were applied to the intensity data (empirical method, Ψ -scan). Positional and thermal parameters were refined by the full-matrix least-squares method. The structure was solved by direct methods and Fourier syntheses. The space group was determined to be the centric $P2_1/a$ from the systematic absences. Computations were performed using the SPD program on an P2P11/44 computer. Crystals are monoclinic, the space group is $P2_1/a$, $a = 10.423(5) \text{ \AA}$, $b = 10.511(3) \text{ \AA}$, $c = 16.896(11) \text{ \AA}$, $\beta = 99.37(5)^\circ$, $V = 1826.4 \text{ \AA}^3$, $Z = 2$, $D(\text{calcd.}) = 1.567 \text{ Mg} \cdot \text{m}^{-3}$, $\mu = 1.22 \text{ mm}^{-1}$, $P(000) = 964$. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.0544$ and $R_w = 0.0670$, $S = 2.512$, $\Delta/\sigma = 0.44$. Final difference Fourier calculations showed a featureless map on which the maximum peak height was 1.291 \AA^{-3} .

2 Results and Discussion

Dibenzoyl peroxide and 2-picolinic acid reacted with metallic copper powder at room temperature giving a blue solution, 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 reaction may be regarded as successive oxidations of Cu with the benzoyl radical, ending with the copper(II) carboxylate compound.

The complex $[\text{Cu}(\text{C}_6\text{H}_5\text{NO}_2)(\text{C}_6\text{H}_5\text{COO})_2]_2$ (Fig. 1) has the expected dimeric form which is bridged via the copper atoms with the carboxylate groups. Two copper(II) ions, two monodentately coordinated 2-picolinic acid and four benzoate form a dimeric complex. The coordination around the copper(II) ion is distorted square-pyramidal. The total angle of $\angle \text{O1-Cu-O3}(88.9^\circ)$, $\angle \text{O1-Cu-O4}'(88.8^\circ)$, $\angle \text{O2'-Cu-O4}'(90.09^\circ)$ and $\angle \text{O3-Cu-O2}'(89.9^\circ)$ is 358° (near 360°). Four oxygen atoms lie in the basal plane with interatomic distances of Cu-O1 1.965 , Cu-O3 1.975 , Cu-O2' 1.957 , Cu-O4' 1.963 \AA , and similar values have been observed in tetrakis (acetato) bis (triph-

enylphosphine) dicopper(II) (av. 1.956 Å)¹¹. The nearest neighbours of the copper atom are the four oxygen atoms of the bridging benzoate ligands in a square planar arrangement. A squarebased pyramidal arrangement about the copper atom is completed by the nitrogen of the 2-picolinic acid ligand at 2.110(8) Å from the copper atom. The copper atom lies 0.21 Å out of the plane defined by the four oxygen atoms, towards the nitrogen atom. The eight-membered ring of C1 O1 Cu O2' C1' O1' Cu' O2 (the sum of inter angle is 1080.2°) and O4' Cu O3 C2 O4 Cu' O3' C2' (the sum of inter angle is 1080.2°) are in the basal plane conformation. The dihedral angle is 90.1°. The C-O distances (1.24, 1.27 Å) and C-C-O

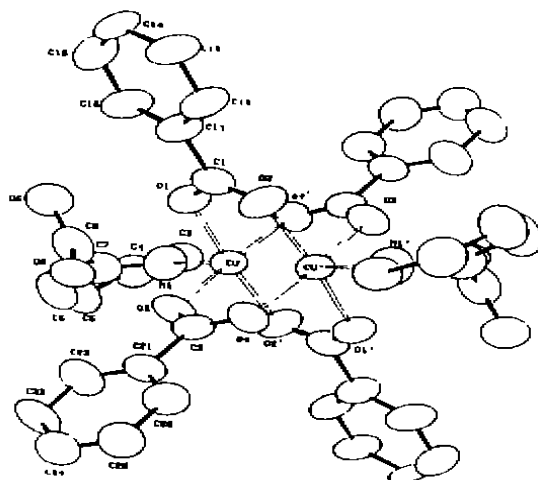


Fig. 1 ORTEP stacking of $[Cu(C_6H_4NO_2)(C_6H_5COO)_2]_2$

angles (118, 125°) in 2-picolinic acid are in agreement with those reported for C6D5COOH (C-O distances 1.26, 1.27 Å, C-C-O angles 118, 119°)¹². The binuclear copper(II) molecular possesses a centre of symmetry. The copper atoms are pentacoordinate (one nitrogen, belong to 2-picolinic acid, and four oxygen to bridging carboxyl groups ligands). Bond distances and angles of the title complex are listed in Table 1; final fractional coordinates are listed in Table. 2

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

atom	distance	atom	distance	atom	distance
Cu-O1	1.963(7)	Cu-O3	1.975(6)	Cu-N1	2.110(8)
Cu-Cu'	2.618(1)	O1-C1	1.257(10)	O2-C1	1.243(12)
O1-C2	1.259(10)	O4-C2	1.229(11)	C1-C11	1.511(14)
N1-C3	1.33(2)	N1-C7	1.42(3)	C8-O6	1.27(9)
C8-O5	1.24(9)	C7-C8	1.45(7)	C6-C7	1.39(4)
C5-C6	1.25(5)	C4-C5	1.46(5)	C2-C4	1.47(3)
Cu-O2	1.957(1)	Cu-O4'	1.963(1)	O2-Cu'	1.956(7)
O1-Cu'	1.962(6)	Cu'-O1'	1.965(6)	Cu'-O3'	1.976(6)
angle	(°)	angle	(°)	angle	(°)
O1-Cu-O3	88.9(3)	O1-Cu-N1	97.2(3)	O3-Cu-N1	94.4(3)
Cu-O1-C1	120.2(6)	Cu-O3-C2	122.3(6)	Cu-N1-C3	126.1(9)
Cu-N1-C7	117.0(1)	C3-N1-C7	117.0(1)	O1-C1-O2	127.0(4)
O1-C1-C11	115.2(8)	O2-C1-C11	117.7(7)	O3-C2-O4	126.0(9)
O3-C2-C21	115.9(8)	O4-C2-C21	118.0(8)	N1-C3-C4	112.0(2)
N1-C7-C6	126.0(2)	N1-C7-C8	117.0(3)	C7-C8-O5	118.0(5)
C7-C8-O6	125.0(5)	O5-C8-O6	118.0(7)	C6-C7-C8	117.0(3)
O1-Cu-Cu'	85.7(2)	O1-Cu-O2'	168.9(2)	O1-Cu-O4'	88.8(2)
O3-Cu-Cu'	84.0(2)	O3-Cu-O2'	89.9(2)	O3-Cu-O4'	168.2(2)
N1-Cu-Cu'	176.7(3)	N1-Cu-O2'	93.9(3)	N1-Cu-O4'	97.3(3)
Cu'-Cu-O2'	83.16(4)	Cu'-Cu-O4'	84.27(4)	O2'-Cu-O4'	90.09(5)
C1-O2-Cu'	124.0(6)	C2-O4-Cu'	123.4(6)	Cu-Cu'-O2	83.2(2)
Cu-Cu'-O4	84.3(2)	Cu-Cu'-O1'	85.7(3)	Cu-Cu'-O3'	84.0(2)
O2-Cu'-O4'	90.1(3)	O2-Cu'-O1'	168.9(2)	O2-Cu'-O3'	89.9(2)
O4-Cu'-O1'	88.8(2)	O4-Cu'-O3'	168.2(2)	O1'-Cu'-O3'	88.9(1)

Table 2 Final Fractional Coordinates for the Complex

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B/Å²</i>	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B/Å²</i>
Cu	0.4089(1)	0.0511(1)	0.94652(6)	3.42(2)	C21	0.300(1)	-0.3303(9)	0.9844(5)	4.2(2)
O1	0.3284(7)	0.1052(6)	1.0381(3)	4.5(1)	C22	0.178(1)	-0.338(1)	0.9406(7)	6.3(3)
O2	0.4849(7)	0.0173(6)	1.1288(3)	5.0(2)	C23	0.113(1)	-0.453(1)	0.9320(8)	8.3(3)
O3	0.3225(7)	-0.1162(6)	0.9496(4)	4.7(2)	C24	0.173(1)	-0.559(1)	0.9671(8)	8.5(3)
O4	0.4796(6)	-0.2032(5)	1.0380(4)	4.1(2)	C25	0.293(1)	-0.553(1)	1.0095(8)	7.2(3)
N1	0.2643(9)	0.1252(9)	0.8555(5)	5.8(2)	C26	0.358(1)	-0.438(1)	1.0201(8)	5.7(3)
C1	0.382(1)	0.0780(8)	1.1083(5)	4.2(2)	C3	0.282(2)	0.216(2)	0.802(1)	6.0(1)
C2	0.374(1)	-0.2064(9)	0.9827(5)	4.0(2)	C4	0.152(3)	0.224(4)	0.736(2)	7.0(1)
C11	0.314(1)	0.1293(9)	1.1738(5)	4.5(2)	C5	0.071(3)	0.134(4)	0.722(2)	6(2)
C12	0.368(1)	0.106(1)	1.2521(6)	6.7(3)	C6	0.040(13)	0.066(3)	0.784(2)	8(1)
C13	0.308(1)	0.154(1)	1.3138(6)	9.0(4)	C7	0.135(3)	0.080(3)	0.853(1)	6.9(4)
C14	0.194(2)	0.223(1)	1.2955(7)	9.6(4)	C8	0.097(4)	0.045(5)	0.928(1)	6(1)
C15	0.142(1)	0.248(1)	1.2188(7)	8.1(3)	O5	0.040(8)	0.125(6)	0.963(4)	7(3)
C16	0.202(1)	0.200(1)	1.1582(6)	6.0(3)	O6	0.122(7)	-0.079(7)	0.966(3)	6(5)

There have been many structural reports concerning bridged binuclear copper (I) compounds^[1], similar to the present complex. The carboxylate bridged Cu...Cu distance of the present compound is found to be 2.618(1) Å, which is comparable to that in tetrakis (formato)-bis(γ-picoline) dicopper (II), 2.655(1) Å^[16].

The five coordinate atoms form a square pyramid with N atom to 2-picolinic acid at the apical position. The basal plane (the four oxygens of the bridging benzoate ligands) forms an almost perfect square. The octahedral environment about the copper atom is completed by the other copper atom of the dimer. The C-O distances in the complex are not significantly different, (av. 1.247 Å), and possess comparable values to those in other acetate-bridging dicopper complex^[1]. All other bond distances and angles are within normal ranges.

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

2.1 IR

The benzoate may coordinate to a metal ion in one of the following modes: unidentate, bidentate and bridging. The IR data shows the existence of the bridging benzoate through the observation of characteristic absorption bands (1600 ~ 1400, 950 ~ 700, 500 ~ 600 cm⁻¹)^[1]. The IR of the [Cu(C₆H₅NO₂)(C₆H₅COO)₂]₂ 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^[1].

In this complex exhibits carboxylate stretches at 1568 and 1402 cm⁻¹, respectively, where (ν_{as} - ν_{sym}) 166 cm⁻¹, consistent with a bridging mode^[1]. In the range 950 ~ 700 and 500 ~ 600 cm⁻¹, there disappear the characteristic absorption bands of δ_{C=O} and π_{C=O}, respectively. These are the characteristics of the typical bridging coordination benzoate^[16]. They are consistent with the results of the crystal structure of the complexes. The bands were assigned to the ν_{C=O} vibrations 277 cm⁻¹ and ν_{C-H} vibrations 308 cm⁻¹, respectively^[16].

The observed absorption band maxima in the electronic spectra, as well as the IR spectra, agreed with those in the literature^[16].

2.2 Electronic Spectroscopy

The ultraviolet-visible spectras are complex. The absorption peaks ($\lambda < 350$ nm) belong to $\pi-\pi^*$ (or $n-\pi^*$) orbital transition of benzoate and ligands. The wide bands (670 nm) belongs to $d-d$ absorption bands of ligand-field. Therefore, the copper(II) atom in the complex is in the square pyramid configuration. 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.

2.3 Thermal Analysis of Complexes

The TG-DTA thermogram (Fig 2) of the complex reveals that the pyrolytic decomposition takes place in two steps. The first one corresponds to a weight loss of 31.4% and is probably due to decomposition of the ligand 2-piclinic acid (loss of weight calculated 28.7%). The decomposition process is confirmed by a strong endothermic peak at 279~302°C. The second step corresponds to, in the 302~500°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 23.0%, calc. 18.6%). The DTA curve shows characteristic exothermic peaks at 302~500°C.

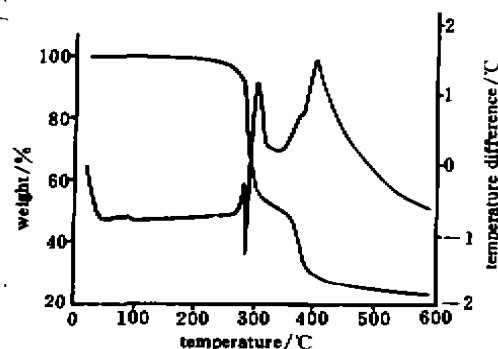


Fig. 2 TG and DTA of $[\text{Cu}(\text{C}_6\text{H}_5\text{NO}_2)(\text{C}_6\text{H}_5\text{COO})_2]_2$

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

References

- [1] Collman J. P., Hegedus L. S. *Principles and Applications of Organotransition Metal Chemistry*. University Science Books, Mill Valley, California, 1980, 176.
- [2] Yang, Ruina et al *Chinese J. Chem.*, 1997, 15(1), 76.
- [3] Pedersen C. J. *J. Am. Chem. Soc.*, 1967, 89, 7017.
- [4] Koman M., Valingura G., Ondrejovic G. *Acta Cryst.*, 1988, C44, 601.
- [5] Feld R., Lehmann M. S., Muir K. W., Speakman J. C. *Z. Kristallogr.*, 1981, 157, 215.
- [6] Yamanaka M., Uekusa H., Ohba S. *Acta Cryst.*, 1991, B47, 344.
- [7] Kazuo Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. John Wiley and Sons, New York, 1970, 230.
- [8] Mehrotra R. C., Bohra R. *Metal Carboxylates*, Academic Press, New York, 1983, 53.
- [9] Melnik M., Mrozinski J. *J. Mol. Struct.*, 1982, 78, 85.