



Original Research article

The Bis(4-methoxy-2-hydroxybenzophenone) copper(II) Complex Used as a New Precursor for Preparation of CuO Nanoparticles



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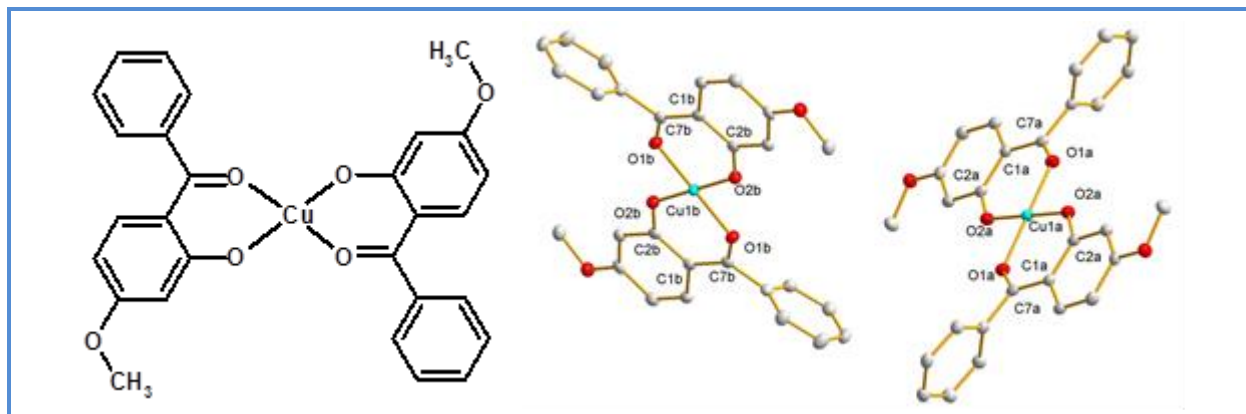
Copper(II) complex
Square-planar geometry
X-ray diffraction
CuO nanoparticles

ABSTRACT

In this study, the reaction of 4-methoxy-2-hydroxybenzophenone (HL) with copper(II) nitrate three hydrate in a 1:2 molar ratio in methanol as solvent resulted in the formation of the complex CuL₂. In order to prepare a suitable single crystal, slow evaporation technique was used, while for preparing complex nanoparticles, assisted ultrasound was used. Crystal structure of CuL₂ was determined by single crystal X-ray diffraction. A square-planar geometry was found for CuL₂. Finally, the complex was calcinated at 600 °C for 2.5 h. The final residue was CuO nanoparticles which were characterized by SEM and XRD. There is no peak for impurity in the XRD pattern.

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Graphical Abstract



Introduction

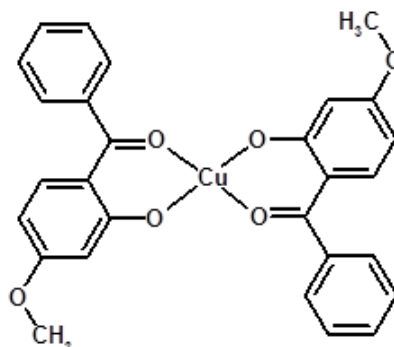
Complexes containing the substituted salicylaldehyde attract continuing attention for their structural diversity and interesting thermal and kinetic properties [1-7]. The substituted salicylaldehyde can coordinate to various transition-metal ions as a bidentate NO ligand in the mono-anionic form, and form various geometries such as square-planar [7], square-pyramidal [7] and octahedral [2]. For example, Zianna *et al.*, [2] reported octahedral complexes with the formula $[\text{Zn}(5\text{-NO}_2\text{-salo})_2(\text{CH}_3\text{OH})_2]$ and a square-planar complex $[\text{Cu}(5\text{-CH}_3\text{-salo})_2]$, and square-pyramidal complex $[\text{Cu}(5\text{-OCH}_3\text{-salo})_2(\text{H}_2\text{O})]$ [7].

In recent years, many articles have been report on the use of complexes for preparing metal oxide nanoparticles by thermal decomposition methods [8-13]. The temperature used in most papers is about 500 °C [8-12] *i.e.*, Yazdan Parest and Morseli [8] prepared zinc oxide nanoparticles at 400 °C for 4 hours from the zinc(II) coordination polymer $[\text{Zn}_3(\text{tza})_3(\text{H}_2\text{O})_3]_n$. Using this method, they prepared a spherical zinc(II) oxide nanoparticle with an average particle size of about 40 nm. Hosny and Dahshan [9] prepared spherical nanoparticles of manganese oxide (Mn_3O_4) from the thermal decomposition of manganese complexes at 500 °C. The obtained particle size is in the range of 39-90 nm.

Recently, many reports have been made on the preparation of copper oxide nanoparticles due to their applications and properties, such as electrocatalytic [14], antioxidant and antibacterial [15], as sensor for electrochemical determination of dopamine [16], photoelectrochemical water splitting [17] and optical properties [18].

Herein, we report the use of 4-methoxy-2-hydroxybenzophenone (HL) to prepare square-planar complex CuL_2 (Scheme 1). The complex was characterized by elemental analyses and single-crystal X-ray diffraction analysis. Nanoparticles of the complex were also prepared using ultrasonic baths. Finally, the complex was thermally decomposed at 600 °C for 2.5 h in order to obtain CuO nanoparticles. At

lower temperatures and in less time, we failed to supply nanoparticles. This method is simple and inexpensive and can be used to prepare other metal oxide nanoparticles.



Scheme 1. Chemical structure of CuL_2

Experimental

Material and methods

All reagents and solvents were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN-O rapid analyzer, and results agreed with the calculated values. Fourier transform infrared (FT-IR) spectra were recorded on a KBr disk on an FT-IR PerkinElmer spectrophotometer. X-ray powder diffraction (XRD) pattern of the complex was recorded on a Bruker AXS diffractometer D8 ADVANCE with $\text{Cu-K}\alpha$ radiation with nickel beta filter in the range $2\theta=10^\circ\text{--}80^\circ$. The scanning electron microscopy (SEM) images were obtained from a Philips XL-30ESEM.

Synthesis of single crystals of CuL_2

A methanolic solution of 4-methoxy-2-hydroxybenzophenone (HL) (0.02 mmol) was added with stirring and heating (60°C) to a solution of copper(II) acetate monohydrate (0.01 mmol). The resulting solution was refluxed for 2 hours. After slow evaporation of the solution for several days, suitable crystals of CuL_2 appeared. They were filtered off and washed with cold methanol. Anal. Calcd. for $\text{C}_{28}\text{H}_{22}\text{Cu}_1\text{O}_6$ (CuL_2): C, 64.86; H, 4.25%. Found; C, 64.81.; H, 4.19%.

Synthesis of nanoparticles of CuL_2

A methanolic solution of 4-methoxy-2-hydroxybenzophenone (HL) (0.02 mmol) was added with stirring and heating (60°C) to a solution of copper(II) acetate monohydrate (0.01 mmol). The resulting solution was treated in a ultrasonic bath for 30 min. The resulting nanoparticles of CuL_2 were filtered off and washed with cold methanol. Anal. Calcd. for $\text{C}_{28}\text{H}_{22}\text{Cu}_1\text{O}_6$ (CuL_2): C, 64.86.; H, 4.25%. Found; C, 64.93; H, 4.32%.

Synthesis of CuO nanoparticles

The complex CuL_2 in the form of nanoparticles was loaded into a platinum crucible, placed in an oven and heated to 600 °C at a rate of 10 °C/min in air. After keeping the sample at the final temperature of 600 °C for 2.5 h, nanoparticles of CuO were obtained. Our efforts to produce pure copper oxide nanoparticles were not fruitful at lower temperatures. The final products were washed with ethanol, dried and characterized by FT-IR, XRD and SEM. FT-IR (KBr, cm^{-1}): 3430 and 1615 (H-OH), 510 (Cu-O).

X-ray structure determination

Suitable single crystal of the dimensions 0.07 mm×0.04 mm×0.02 mm was chosen for X-ray diffraction study. Crystallographic measurements was done at 95 K with a four circle CCD diffractometer super nova of Rigaku oxford diffraction, using Cu-K α radiation from a micro-focus sealed tube collimated by mirrors. As a detector we used the CCD detector Atlas S2. The crystal structure was solved by charge flipping with the program SUPERFLIP [19] and refined with the Jana 2006 program package [20] by full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by Diamond 4.0 [21]. All hydrogen atoms were discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice, H atoms bonded to C were kept in ideal positions with C-H=0.96 Å and with U_{iso} (H) set to $1.2U_{\text{eq}}$ (C). All non-hydrogen atoms were refined using harmonic refinement. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

Table 1. Crystallographic data and structural refinement details of CuL_2

Formula weight	$\text{C}_{28}\text{H}_{22}\text{Cu}_1\text{O}_6$
Formula weight	518
Crystal system	Triclinic
Space group	$P-1$
a, Å	5.5570 (2)
b, Å	10.4465 (3)
c, Å	20.3534 (7)
α , deg	103.533 (3)
β , deg	90.085 (3)
γ , deg	104.022 (3)
V, Å ³	1112.38 (7)
Z	2
μ , mm ⁻¹	1.77
R_{int}	0.023
S	1.28
Measured reflections	6943
Independent reflections	4377
Parameters	319
Reflections with $I > 3\sigma(I)$	3542
$R(F^2 > 2\sigma(F^2))$	0.035
$wR(F^2)$	0.099
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$	0.30, -0.37

Results and discussion

Structure description of CuL₂

Two distinct neutral complex molecules of the title compound with the atomic numbering scheme are shown in Figure 1.

The selected bond distances and angles are given in Table 2. The compound 4-methoxy-2-hydroxybenzophenone acts as a deprotonated bidentate ligand coordinated to the copper(II) ion in trans form. The geometry around the copper(II) ion in CuL₂ is square planar. The Cu-O distances are in the ranges of 1.88 to 1.93 Å and the intrachelate and intrachelate O-Cu-O angles are 87.09 (7), 92.91 (7) and 180.0 (5)° [7].

Using the values of the bond angles around the ion center, and using the following equation $\{\tau = (\alpha - \beta) / 90\}$, we can determine the suitable geometry for the coordination number of 4. α and β are the largest and lowest bond angles, respectively. For $\tau=0$, the geometry around the ion center is tetrahedral and for $\tau=1$, the geometry around the ion center is square planar [22]. In this complex, $\tau=1.03$, then the geometry around the copper ion is square planar. However, the unequal bond lengths and the angles around the copper ion center, confirmed the distortion from the ideal square planar.

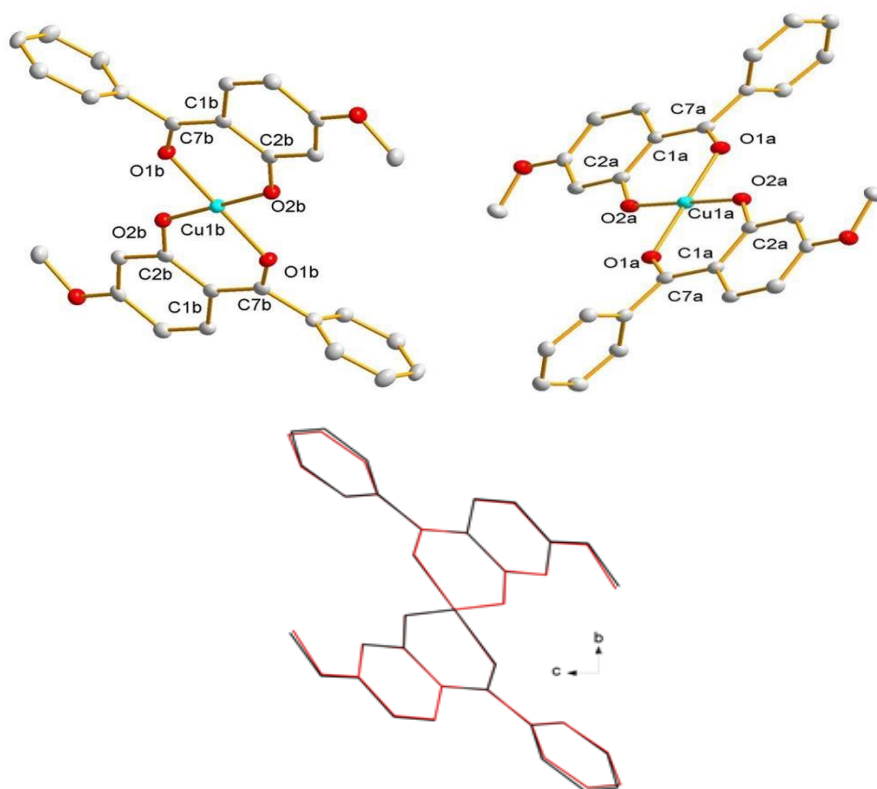


Figure 1. The two independent molecular structures of the title compound and overlay of both molecules, a) black, b) red

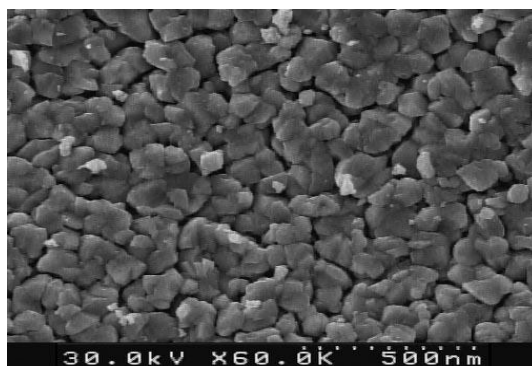
Table 2. Selected bond distances and angles (Å, °)

Cu1a-O1a	1.9303 (15)
Cu1a-O2a	1.8867 (16)
Cu1b-O1b	1.9332 (16)
Cu1b-O2b	1.8872 (15)
O1b-Cu1b-O1b	180.0 (5)
O2b-Cu1b-O2b	180.0 (5)
O1b-Cu1b-O2b	92.88 (6)
Cu1a-O2a-C2a	127.84 (12)
O1b-Cu1b-O2b	87.12 (6)
Cu1b-O1b-C7b	127.14 (16)
Cu1b-O2b-C2b	127.69 (16)
O1a-Cu1a-O1a	180.0 (5)
O2a-Cu1a-O2a	180.0 (5)
O1a-Cu1a-O2a	92.91 (7)
O1a-Cu1a-O2a	87.09 (7)
Cu1a-O1a-C7a	127.22 (13)

Interesting feature of the crystal structure is the similarity of both symmetry-independent molecules. Figure 1 shows their overlay calculated by crystal CMP program [23] and indicates that the molecules are almost identical. In order to test whether the molecules are really identical, we used the rigid body tool of Jana 2006 and refined only one molecule in two positions defined by a translation vector and three independent rotations, using the TLS tensors for description of rigid body displacement parameters. This refinement smoothly converged at $R=0.0522$ (an increase by ~ 0.02) and $S=1.90$ (an increase by ~ 0.6), resulting in the same message that the molecules are nearly identical. However, diffraction pattern does not allow to use a smaller or more symmetrical unit cell, so the identical symmetry independent molecules should be considered a matter of fact.

Nanoparticles of the complex

Ultrasonic bath assisted preparation of CuL_2 resulted in uniformly shaped nanoparticles shown in the SEM image (Figure 2). Figure 2 shows that the size of the complex particles is larger than 100 nanometer.

**Figure 2.** SEM image of CuL_2

CuO nanoparticles

We prepared CuO nanoparticle *via* thermal decomposition of CuL_2 at 650 °C for 2.5 h (Figure 3). Our efforts to produce nanoparticles at lower temperatures and in less time were useless. High temperature and long time causes the nanoparticles to become larger, because in this case the nanoparticles are sticking together.

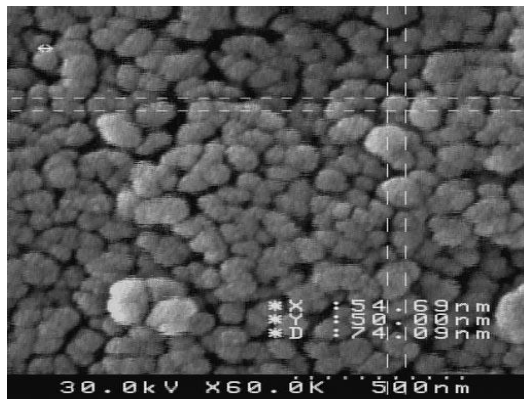


Figure 3. SEM image of CuO nanoparticles

(Figure 3) shows the SEM image of CuO nanoparticles that exhibit uniform shapes. Although they have different dimensions, comparing Figures 2 and 3, the size of copper oxide nanoparticles is smaller than the size of the nanoparticles of the complex itself.

In the FT-IR spectrum copper oxide nanoparticles, the two-peaks in the 3430 and 1615 cm^{-1} regions represent the H-OH stretching of water-adsorbed molecules on the surface of nanoparticles [16]. The sharp peak at about 510 cm^{-1} is a characteristic peak of Cu-O stretching [16-24].

(Figure 4) shows the XRD pattern of CuO nanoparticles that can be fully indexed based on the monoclinic CuO (JCPDS: 45-0937) [25]. XRD results, thus, indicate the complete conversion of CuL_2 to CuO. No obvious impurities were detected, indicating the high phase purity of the as-prepared samples. Also, the broadening of all the peaks in the XRD pattern indicates that the crystallites are small. Based on the Scherrer's equation, the particle size was about 45 nm.

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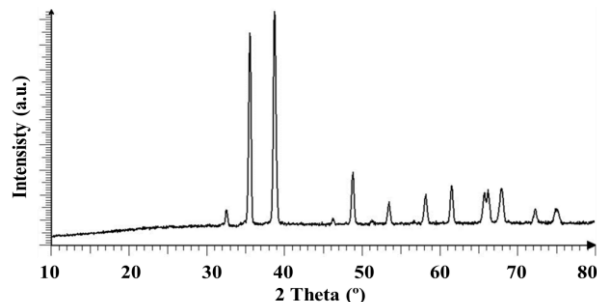


Figure 4. XRD pattern of CuO nanoparticles

Supplementary materials

CCDC 1874702 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conflict of Interest

We have no conflicts of interest to disclose.

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