



PERGAMON

Polyhedron 21 (2002) 2017–2020



POLYHEDRON

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# Copper(II) methoxide: direct solventothermal synthesis and X-ray crystal structure

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Received 15 February 2002; accepted 18 June 2002

## Abstract

Copper methoxide has been prepared under fairly mild solventothermal conditions by direct reaction of copper(II) acetate monohydrate and methanol. The product has been structurally characterized for the first time by single crystal X-ray diffraction and found to possess a novel infinite one-dimensional chain structure in which copper atoms in distorted square planar coordination environments are linked by bridging methoxide ligands. The conversion of copper acetate to copper methoxide is essentially quantitative. The major byproduct of the synthesis is methyl acetate. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Solventothermal synthesis; Crystal structures; Coordination polymers; Copper methoxide; Single crystals

## 1. Introduction

The first report describing the synthesis and isolation in pure form of copper(II) methoxide was made by Brubaker and Wicholas [1] in 1965. In this report, copper methoxide was prepared in 89.5% yield by reaction of lithium methoxide and CuCl<sub>2</sub> in methanol and characterized by elemental analysis and infrared spectroscopy. A three-dimensional extended structure for copper(II) methoxide was proposed, based upon spectral properties and upon its unusual insolubility (for an alkoxide) in organic solvents and low volatility. In the same year Costa et al. [2] reported preparation of copper methoxide via decomposition of CuCH<sub>3</sub> in the presence of air and by reaction of CuBr<sub>2</sub> with NaOCH<sub>3</sub> in methanol. In this report, copper(II) methoxide was characterized by elemental analysis and infrared spectroscopy. While the authors obtained a powder X-ray diffraction pattern of products, no unit cell or data was reported. It was only reported that copper oxide and

metallic copper were absent, based upon this unspecified powder diffraction data. Thus, it was not possible to compare our results (via a simulated powder pattern) to any diffraction data in Ref. [2]. Copper(II) methoxide has also been prepared by adding pyridine to a suspension of metallic copper in methanol under an oxygen atmosphere [3]. In addition, copper methoxide has been identified as an intermediate existing within a zeolite framework during CuY-catalyzed oxidative carbonylation of methanol [4].

We now report the direct synthesis of copper(II) methoxide (**1**) from copper(II) acetate monohydrate and methanol under solventothermal conditions. We have determined the structure of copper(II) methoxide via single crystal X-ray methods. This is the first definitive structural characterization of this coordination polymer, and the synthesis does not require any inert-atmosphere techniques or drying of solvent until the product isolation stage. Secondary characterization has been accomplished by comparison of IR spectra to those that have been published previously [1,2]. The route by which copper methoxide forms in the present study has been established through analysis of the byproducts in solution after reaction.

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## 2. Experimental

Methanol (99.8%, anhydrous), copper(II) acetate monohydrate (98 + %) and nitric acid (trace metal grade) were obtained from commercial sources and used as received. UV–Vis spectra were recorded using matched quartz cells on a Shimadzu UV2101 PC spectrophotometer. IR spectra were recorded on a Mattson Galaxy 5000 FT-IR spectrometer. GC-MS data were obtained using a Varian Saturn 2100D instrument, and inductively coupled plasma emission data were recorded and analyzed using a Thermo Jarrell Ash Atom Scan 25 instrument and associated software.

### 2.1. Synthesis of copper(II) methoxide

In a typical experiment, a glass vial was charged with 24.5 mg (0.123 mmol) of copper(II) acetate monohydrate and 5.0 ml of methanol. After stirring, the vial was placed into a Teflon-lined stainless steel autoclave and heated to 110 °C for three days. Upon opening the autoclave, dark purple block-shaped crystals of **1** were observed on the bottom and sides of the vial. No other solid product was evident, and the supernatant liquid was colorless. The vial containing the crystals and mother liquor was capped with a rubber septum and attached to the Schlenk line via a needle. Under argon, the mother liquor was withdrawn and analyzed by UV–Vis and GC-MS. These experiments clearly indicated the presence of methyl acetate in the mother liquor. The crystals remaining in the vial after removal of the mother liquor were washed with several 5 ml portions of methanol under argon. No observable change occurred during the washing or subsequent evacuation of the vial.

### 2.2. Spectroscopic characterization of copper(II) methoxide

A sample of the washed crystalline material described above was ground under methanol to produce a fine slurry. Several drops of the slurry were placed on a sodium chloride plate in an argon-filled chamber that was subsequently evacuated. When the methanol had evaporated from the slurry, the chamber was filled with argon and brought to the IR spectrometer, the sample cavity of which had been purged with nitrogen gas. The salt plate was mounted in the spectrometer and a spectrum matching that of copper(II) methoxide [1,2] was recorded. The sample cavity was then opened to the air and spectra were recorded at approximately five-minute intervals, during which time the bands ascribed to copper methoxide were replaced by a broad O–H band typical of a hydrogen-bonded O–H stretch and other unidentified signals.

### 2.3. Inductively coupled plasma emission spectroscopic analysis.

The synthesis of **1** was carried out using a 24.7 mg (0.124 mmol) sample of copper(II) acetate monohydrate. After reaction, the mother liquor was transferred to a Schlenk flask that was then subjected to dynamic vacuum until no solvent was evident. The residue was dissolved in nitric acid and diluted to 50.00 ml with de-ionized water. Analysis of this solution against a 10.00 ppm Cu standard indicated a Cu concentration of 0.157 ppm with a standard deviation of 0.005 ppm. This corresponds to  $1.24 \times 10^{-4}$  mmol Cu in the entire analyte solution.

### 2.4. Crystallography

Crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). A purple block-shaped crystal with approximate dimensions  $0.45 \times 0.14 \times 0.12$  mm, obtained directly from the reaction vial, was mounted under oil on the tip of a glass capillary. The crystal was mounted in a stream of nitrogen gas at 173(2) K and centered in the X-ray beam.

Crystal Data: C<sub>2</sub>H<sub>6</sub>CuO<sub>2</sub> (formula weight = 125.61), tetragonal, space group  $P4_2/mbc$ ,  $a = 8.1848(6)$  Å,  $c = 5.8770(4)$  Å,  $V = 393.71(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calc}} = 2.119$  g cm<sup>-3</sup>,  $F(000) = 252$ ,  $\mu$  (Mo K $\alpha$ ) = 5.356 mm<sup>-1</sup>. Initial cell constants were obtained from three series of  $\omega$  scans at different starting angles. Each series consisted of 50 frames collected at intervals of 0.3 in a 15° range about  $\omega$  with an exposure time of 20 s per frame. The final cell constants were calculated from a set of 1084 strong reflections. Data were collected by use of the hemisphere data collection routine. A total of 3205 data were harvested by collecting three sets of 30-s frames with 0.3° scans in  $\omega$ . Data were corrected for Lorentz and polarization effects. An absorption correction was performed and was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [5]. Systematic absences in the diffraction data were consistent with the space groups  $P4_2bc$  and  $P4_2/mbc$ . The  $E$ -statistics strongly suggested the centrosymmetric space group  $P4_2/mbc$  that yielded chemically reasonable and computationally stable refinement results [6]. A solution by direct methods provided most of the non-hydrogen atoms from the  $E$ -map. The remaining non-hydrogen atoms were located in an alternating series of least-squares and difference Fourier maps. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. A total of 3205

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