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

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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.

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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 CuCl₂ 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 CuCH₃ in the presence of air and by reaction of CuBr₂ with NaOCH₃ 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 fiveminute 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 deionized 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 1.24×10^{-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 α radiation ($\lambda = 0.71073$ Å). A purple blockshaped crystal with approximate dimensions $0.45 \times$ 0.14×0.12 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: $C_2H_6CuO_2$ (formula weight = 125.61), tetragonal, space group $P4_2/mbc$, a = 8.1848(6) Å, c =5.8770(4) Å, V = 393.71(5) Å³, Z = 4, $\rho_{calc} = 2.119$ g cm⁻³, F(000) = 252, μ (Mo K α) = 5.356 mm⁻¹. Initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 50 frames collected at intervals of 0.3 in a 15° range about ω 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 ω . 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 $P4_{2}bc$ 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 Emap. 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

reflections were collected, 224 of which were independent [$R_{int} = 0.0300$] in the range $3.52^{\circ} < \Theta < 26.38^{\circ}$. The data were 100% complete over this range. The final least squares refinement on F^2 yielded $R_1 = 0.0204$ ($wR_2 = 0.0713$) for 179 reflections having $I > 2\sigma(I)$, where $wR_2 = \Sigma [w(F_o^2 - F_c^2)] / \Sigma [(wF_o^2)^2]^{1/2}$; $R_1 = \Sigma \Delta / \Sigma (F_o)$, $\Delta = |(F_o - F_c)|$. The Cu atom occupies three crystallographic twofold axes while the carbon and oxygen atoms reside on a crystallographic mirror plane.

3. Results and discussion

We have found that treatment of copper(II) acetate monohydrate with methanol for three days at 110 °C produces exceptionally well-formed deep purple blockshaped crystals of copper(II) methoxide with no other solid products. These crystals are indefinitely stable under the mother liquor or pure methanol at room temperature. They also appear to be stable for at least several hours under argon or vacuum. In the air in absence of methanol, the crystals decompose rapidly, undergoing an irreversible color change to light blue. Interestingly, if the amount of copper acetate reacting in 5.0 ml of methanol is raised above 25 mg, the yield of purple crystals is drastically decreased and a large amount of uncharacterized brown/black solid forms. Further, no reaction is observed if the same starting material is left to stand in methanol under argon for 11 days, indicating that solventothermal conditions are necessary for the facile synthesis of 1 by this reaction.

3.1. Description of the crystal structure of copper(II) methoxide

After preliminary identification of the identity of the purple crystalline product as copper(II) methoxide, confirmation was achieved via single crystal X-ray methods. In the structure of 1, infinite one-dimensional chains of copper atoms with bridging methoxide ligands run parallel to the crystallographic c-axis in the tetragonal space group $P4_2/mbc$. The copper atoms in 1 are each coordinated by four oxygen atoms in a distorted square planar fashion. The methyl groups on either side of the one-dimensional chain tip in alternating directions away from the mean copper-oxygen plane in a 'zig-zag' arrangement, and the copper atoms are arranged in a linear fashion with respect to one another. A segment of this coordination polymer is shown in Fig. 1. Fig. 2 is a view down the crystallographic c-axis showing the orientation of the chains with respect to one another. Fig. 3 presents a view looking down the crystallographic a axis, illustrating the orientation of the methyl groups in 1 with respect to the linear arrangement of copper atoms. Selected bond distances and angles are reported in Table 1.



Fig. 1. A section of the infinite one-dimensional chain in 1, with ellipsoids drawn at the 50% probability level.



Fig. 2. A view down the crystallographic c-axis in the lattice of 1.



Fig. 3. A view down the crystallographic *a*-axis in the lattice of 1.

The bridging of copper atoms by methoxide ligands is a common structural motif, but the infinite chain structure determined for **1** is novel. The structure of **1** can be thought of as the most basic of all methoxidebridged Cu coordination compound structures. A search of the Cambridge Structural Database [7] for compounds containing methoxide ligands bridging copper

Table 1 Selected bond lengths (Å) and bond angles (°) for 1 $\!\!\!\!$

Bond lengths $Cu(1) = O(1)$	1 915(1)	O(1) = C(1)	1 417(3)
Bond angles	1.915(1)	0(1) 0(1)	1.417(5)
O(1)-Cu(1A)-O(1A) O(1)-Cu(1A)-O(1D)	100.5(1) 79.80(9)	C(1) - O(1) - Cu(1)	124.22(8)

atoms, limited to structures with final R values of 5% or lower and no disorder yielded 26 hits. Among these structures, the average Cu–O distance was 1.93(2) Å and the average Cu–Cu separation 3.0(1) Å. Both the Cu–O bond distance and Cu–Cu separation in 1, 1.915(1) and 2.9385(2) Å, respectively, compare well with these parameters.

3.2. Discussion of the synthetic reaction and products

The only solid product of the synthesis is 1, as confirmed by IR spectroscopy. Analysis of the mother liquor by inductively coupled plasma emission spectroscopy showed only a minute trace of copper, corresponding to about 0.1% of the copper in the starting material. This indicates that the conversion of copper(II) acetate to copper(II) methoxide is essentially quantitative, as there are no reasonable volatile copper-containing products. A UV-Vis spectrum of the mother liquor was transparent in the visible region, showing only an absorbance attributable to methyl acetate, the presence of which was confirmed by GC-MS. We believe that the methyl acetate forms via a classical condensation reaction whereby methanol and acetic acid react with elimination of water and concomitant formation of the ester. This observation strongly suggests that acetate ions, present in solution due to the use of copper acetate as the copper source, are responsible for deprotonation of methanol. It is not clear what role, if any, copper atoms may play in this process. Nonetheless, the overall pathway by which 1 and methyl acetate form can be summarized as shown in Scheme 1.

This work has confirmed initial suppositions of a methoxide-bridged polymeric structure for copper(II) methoxide [1], well supported from the beginning by observed physical properties. What is not clear is whether the initial suggestion of a three-dimensional coordination polymer (as opposed to the crystallographically-determined one-dimensional structure) was in fact in error, or rather that the present conditions result in the formation of a different phase of copper methoxide than those that had been prepared and characterized previously. This question will be difficult to answer conclusively, as none of the previously

CH ₃ OH ·	$+ CH_3COO^- \leftrightarrows CH_3O^- + CH_3COOH$	
$n(Cu^{2+})$	$+ 2n(CH_3O) \rightarrow [Cu(OCH_3)_2]_n$	
CH ₃ COC	$H + CH_3OH \rightarrow CH_3COOCH_3 + H_2OCH_3 + H_2O$)

Scheme 1.

reported synthetic conditions lead to products that are suitable for complete structural characterization by Xray methods.

The observed stability of **1** under methanol, even in the presence of a significant amount of water (present because of the use of hydrated copper acetate as starting material) is somewhat surprising and worthy of note. The observation that a sample of **1** identified in the nitrogen-purged sample cavity of an IR spectrometer decomposes rapidly upon the introduction of air is, however, consistent with the known air sensitivity of copper methoxide in the absence of solvent.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 178855. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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