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Century-Known Copper Salt Cu(OAc)(OMe) Proven To Be a Unique Magnetic Lattice Composed of Tetranuclear Copper(II) Species with a Rare Binding Mode of the Acetate Anion

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The structure, spectroscopy, and magnetism of a century-old copper salt, Cu(OAc)(OMe), is reported. The crystal structure contains two independent Cu(II) ions, which are both five-coordinated and which are bridged by methoxo and acetate anions to form an infinite 2D network. Thereby the methoxo groups connect Cu1 and Cu2 with their symmetry-generated counterparts $Cu1^i$ and $Cu2^i$, respectively, resulting in Cu···Cu distances of 2.9803(10) and 2.9874(10) Å. Cu1 and Cu2 themselves are bridged via the carboxylate groups of two acetates leading to a Cu1···Cu2 distance of 2.9473(7) Å. The tetranuclear units thus generated are cross-linked via acetate oxygens to form a 2D sheet structure. One of the two independent acetate ligands has a rare binding mode, whereby it acts as a tetradentate *syn-anti*, *syn-anti* bridging ligand. The temperature dependence of the magnetic susceptibility was assigned to be dominated by the very strong antiferromagnetic exchange coupling via bis(μ-methoxo) bridges ($J_1 = -409(1)$ cm^{-1}).

Introduction

A large variety of copper(II) coordination compounds containing alkoxyl or carboxylate bridging anions have been described in the literature during the past years.[1] The interest in this subject resulted from the attractive magnetic and catalytic properties of these compounds.[2−6] The formation of a copper(II) acetate methoxide in impure form was first reported in 1902 by Wislecerus and Stoeber.[7] Very pure (acetato)(methoxo)copper(II) (**1**) was prepared in 1976 by Yampol'skaya et al.[8] Although the authors proposed that the compound obtained is a polynuclear derivative of copper(II) acetate, no definite conclusions related to the structure of the complex were reached.

In this paper, the unique crystal structure and spectral and magnetic properties of an inorganic copper(II) acetate methoxide polymer are presented. Although 1 century has passed since the preparation of this compound has been first reported, no direct proof concerning its detailed structure has been published so far. A difficulty in the crystal structure determination is the small size of the crystals, which makes strong X-ray sources compulsory that were not available until recently. Another problem are the mica type stacking faults of the 2D structure. Only by using the new area detector technology and modern indexing and evaluation software[9,10] this structure could now be solved.

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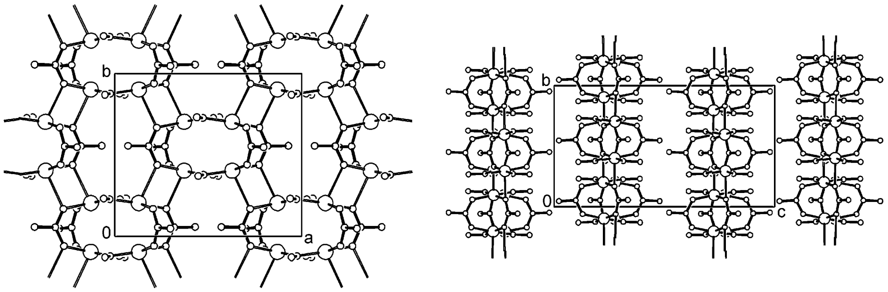

Figure 1. Platon[15] projection of the 2D layer structure of copper(II) acetate methoxide along the crystallographic *c*-axis (left) and *a*-axis (right). Hydrogen atoms are omitted for clarity.

Experimental Section

All starting materials were commercially available and used as purchased. The infrared spectrum of **1** in the 4000−300 cm^{-1} range was recorded on a Bruker 330V IR spectrophotometer equipped with a Golden Gate Diamond. The ligand field spectrum of the solid (300−2000 cm^{-1}, diffuse reflectance) was taken on a Perkin-Elmer 330 spectrophotometer equipped with a data station. Bulk magnetization of a 40.60 mg polycrystalline sample of **1** was measured in the range 5−400 K with a Quantum Design MPMS-5S SQUID magnetometer, in a 1 kG applied field. The data were corrected for the experimentally determined contribution of the sample holder. Corrections for the diamagnetic response of **1**, as estimated from Pascal's constants, were applied.

Synthesis of [Cu(CH$_3$COO)(CH$_3$O)]$_n$ (1). A 0.23 g (1.3 mmol) amount of copper acetate monohydrate was dissolved in anhydrous methanol upon heating, and the resulting turbid greenish-blue solution was filtered. Slow diffusion of diethyl ether into this solution led to a gradual color change to blue. Very small blue rectangular crystals of **1** appeared within a few days. It is worthwhile to mention that only a small fraction of the initial copper acetate is transformed into **1** (the final yield of **1** is at most 10%). Ether diffusion into more concentrated solutions led to the quick appearance of green hexagonal crystals of [Cu$_2$(CH$_3$COO)$_4$(MeOH)$_2$].[11]

X-ray Structure Determination. Most crystals were found to have multiple domains in random orientation. After an intensive search a crystal could be found which consisted of one major and one minor domain. An indexing was achieved using the $\phi-\phi/\chi$ scan method.[9] Only the major domain was then considered for the intensity evaluation[10] leading to a 99.7% completeness up to a resolution of (sin θ)/λ = 0.61 Å^{-1}.

Data are as follows: $C_6H_{12}Cu_2O_6$, fw = 307.24; blue block, 0.06 × 0.06 × 0.03 mm^3; monoclinic crystal system, space group *C*2/*c* (No. 15); cell parameters $a = 11.2752(3)$, $b = 9.7976(3)$, and $c = 17.8504(6)$ Å, $\beta = 93.7004(13)°$, $V = 1967.82(10)$ Å^3, and $Z = 8$; $\rho = 2.074$ g/cm^3; $F_{000} = 1232$. A total of 8376 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode and Mo Kα radiation (graphite monochromator, $\lambda = 0.710\ 73$ Å) at a temperature of 110 K. An absorption correction[12] based on multiple measured reflections was applied ($\mu = 4.32$ mm^{-1}, 0.75−0.88 transmission). The reflections were merged using the program SORTAV,[12] resulting in 1861 unique reflections ($R_{int} = 0.084$), of which 1257 were observed [$I > 2\sigma(I)$]. The structure was solved with automated Patterson methods using the program DIRDIF[13] and refined with the program SHELXL97[14] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters, and hydrogen atoms were introduced in calculated positions and were not refined. There were a total of 127 refined parameters and 0 restraints. R (observed reflections): R1 = 0.0353; wR2 = 0.0797. R (all data): R1 = 0.0608; wR2 = 0.0932. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0455P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. GoF = 0.996. Residual electron density was between −0.71 and 0.74 e/Å^3. The drawings, structure calculations, and checking for higher symmetry were performed with the program PLATON.[15]

Results and Discussion

Crystal Structure Description. Very small blue rectangular crystals of inorganic polymer (acetato)(methoxo)copper(II) (**1**) are formed by ether diffusion into a methanolic solution of copper(II) acetate monohydrate. The coordination polymer represents an intricate infinite 2D network of copper(II) ions in the (001) plane, bridged by (i) didentate acetate anions with *syn-syn* geometry, (ii) methoxide moieties, and (iii) tetradentate *syn-anti*, *syn-anti* acetate anions (Figure 1). To the best of our knowledge, the latter coordination mode of acetate anion has only been observed in a few cases, e.g. in a polymorph of calcium acetate[16] and in $Co_5(OH)_2(O_2CCH_3)_8{\cdot}2H_2O$,[17] and has never previously been encountered in either Cu(II) or Cu(I) complexes. The acetate anion has four lone pairs, which are potential donors for metal coordination. In most cases[18] only two or three of them are actually used to bridge between metal centers. Quite frequently the remaining lone pairs function as acceptors for hydrogen bonds. Thus, this is one of the rare examples in which *each* of the two oxygen atoms acts as a bridge between two metal ions.

The compound crystallizes in the *C*2/*c* space group, with 16 copper ions present/unit cell. The asymmetric unit comprises two crystallographically independent copper ions, one tetracoordinated acetate anion and one dicoordinated acetate anion, and two methoxide groups (Figure 2). The

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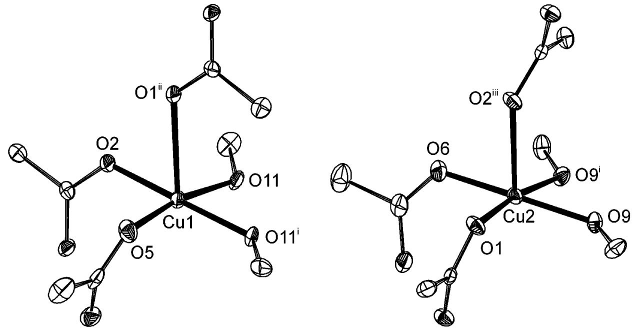

Figure 2. Coordination environments of Cu1 and Cu2 (50% probability level). Hydrogen atoms have been omitted for clarity. Symmetry operations: (i) $1 - x, y, -z$; (ii) $-x, y - 1/2, -z$; (iii) $-x, y + 1/2, -z$.

coordination environments around both copper ions are almost ideal square pyramids, with τ-values[19] of 0.03 for Cu1 and Cu2 (Figure 2). The equatorial plane around the Cu1 ion is formed by the two oxygen atoms O11 and O11^{i} ($1 - x, y, -z$) from two methoxide groups (Cu1$-$O11 1.914(3) Å and Cu1$-$O11^{i} 1.927(3) Å), the oxygen atom O5 from a didentate acetate anion (Cu1$-$O5 1.932(3) Å), and the oxygen atom O2 from a tetradentate acetate anion (Cu1$-$O2 1.968(3) Å). The O$-$Cu1$-$O in-plane cis angles vary in quite a broad range, viz. 76.26(14)° for the O11$-$Cu1$-$O11^{i} angle to 96.27(12)° for the O11$-$Cu1$-$O2 angle. The apical bridging oxygen atom O1^{ii} ($1/2 - x, y - 1/2, -z$) is located at a larger distance (Cu1$-$O1^{ii} 2.543(3) Å). The square plane around the Cu2 ion, similarly, includes the two oxygen atoms O9 and O9^{i} from two methoxide moieties (Cu2$-$O9 and Cu2$-$O9^{i} distances equal to 1.919(3) Å and 1.930(3) Å, respectively), the oxygen atom O6 of a didentate acetate anion at a distance of 1.940(3) Å, and the oxygen atom O1 of the tetradentate acetate anion at a distance of 1.968(3) Å. The apical position is occupied by the bridging oxygen atom O2^{iii} ($1/2 - x, y + 1/2, -z$) from tetracoordinated acetate anion at a distance of 2.558(3) Å. The four in-plane cis O$-$Cu2$-$O angles vary in the same range as for the Cu1 ion, with the smallest angle being O9$-$Cu2$-$O9^{i}, both oxygen atoms originating from two bridging methoxy groups.

Three types of bridging ions and in particular the unusual tetradentate binding mode of the acetate anions (Figure 3) result in the formation of the beautiful two-dimensional network which is schematically presented in Figure 4. It can be best regarded as built from the tetranuclear units of the formal composition [$Cu_4(CH_3COO)_4(CH_3O)_4$], assembled into an infinite array by means of relatively long intermolecular copper$-$oxygen bonds (Cu$-$O distances 2.543(3) and 2.558(3) Å). Each tetranuclear unit can be regarded as a square of four copper ions with crystallographic 2-fold symmetry, bridged by two trans-located pairs of methoxo groups (Cu$-$O$-$Cu angles of 101.81(13) and 101.77(14)°) and two trans-located pairs of acetate ions with the *syn-syn* geometry. The interior angles of the square are 90.05(2) and 89.92(2)°, and the copper$-$copper distances are almost identical (viz. 2.9473(7) Å for both acetate-bridged couples and 2.9803(10) and 2.9874(10) Å for the methoxo-bridged couples). The assembly of tetranuclear units into an infinite 2D array proceeds via eight additional intermolecular Cu$-$O contacts with four adjacent tetramers, resulting in a Cu$\cdots$Cu distance of 3.5295(7) Å for Cu1$\cdots$Cu2^{ii}. Two of the four trans-located acetate anions of each unit are tetracoordinated. Thus, each oxygen atom, besides forming an *intra*molecular short (~1.9 Å) copper$-$oxygen bond via the syn lone pair of electrons, is additionally involved into *inter*molecular long (~2.6 Å) copper$-$oxygen bond, realized via the anti lone pair of electrons.[18] Respectively, the intermolecular bonding is constituted via four pairs of parallel copper$-$oxygen bonds (Figure 4).

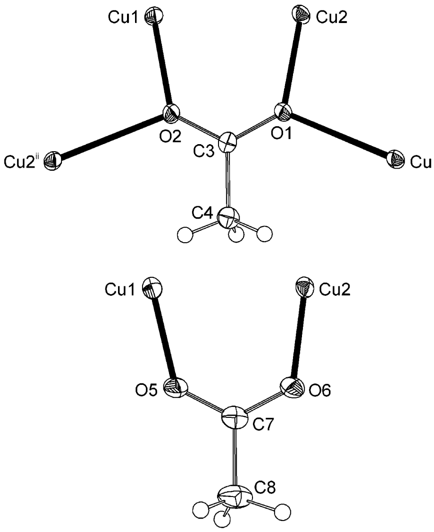

Figure 3. Displacement ellipsoid plot[15] (50% probability level) of the tetradentate (top) and didentate (bottom) acetate anions and the coordinated copper centers. Symmetry operations: (ii) $-x, y - 1/2, -z$; (iii) $-x, y + 1/2, -z$.

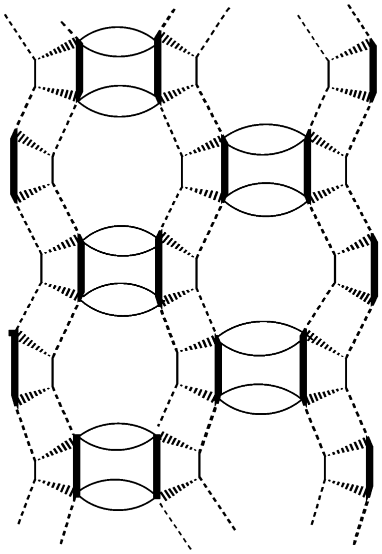

Figure 4. Schematic representation of the infinite 2D network in **1**. Bold lines represent copper$-$copper pairs bridged by didentate acetates with *syn-syn* geometry, solid lines represent tetracoordinated acetate anions, and curved lines represent bridging methoxide groups. Short intramolecular bonds and long intermolecular chain bonds are shown with dashed and hashed wedged lines, respectively.

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Spectroscopic Data. In the IR spectrum of **1**, the band corresponding to $\nu_{as}(CO_2^-)$ of the bridging acetate,[20] observed at 1596 cm^{-1} in the initial dimer copper acetate, is shifted to a lower frequency, viz. 1576 cm^{-1}. In addition, a weaker band is observed at 1526 cm^{-1}. These data are consistent with the values described by Yampol'skaya et al.[8] However, the authors assigned the latter band to the chelating acetate ions whereas, according to the crystal structure, all acetate anions form bridges between two different copper ions. Thus, this band should be attributed to $\nu_{as}(CO_2^-)$ of the tetracoordinated acetate moieties. The intensive band at 1067 cm^{-1} can be assigned to the C−O stretching vibrations of the bridging methoxide groups.[20] The diffusion reflectance spectrum of **1** is characterized by the presence of a single broad band around 15 500 cm^{-1}, which is in a normal range for square-planar-based CuO_4 chromophores.[21]

Magnetic Susceptibility. The temperature dependence of the molar magnetic susceptibility/Cu(II) ion, χ_M, in the temperature range 5−400 K is represented in Figure 4. At 400 K, χ_M is 5.07×10^{-4} $cm^3\ mol^{-1}$, which corresponds to an effective magnetic moment μ_{eff} of 1.47. These values are smaller than the expected ones for uncoupled Cu(II) ions ($\chi_M = 9.37 \times 10^{-4}$ $cm^3\ mol^{-1}$ and $\mu_{eff} = 1.73$; μ_B for $g = 2$). Upon cooling, χ_M decreases to reach a minimum of 3.79×10^{-4} $cm^3\ mol^{-1}$ around 190 K, which indicates the presence of a dominant strong antiferromagnetic interaction in **1**. The broad rounded maximum in the susceptibility curve characteristic of such large antiferromagnetic coupling could unfortunately not be reached at the highest temperature accessible with our experimental setup. Below 190 K, the susceptibility increases with decreasing temperature. This low-temperature tail is thought of arising mainly from a small portion of paramagnetic impurities. The data below 150 K are indeed well-fitted by a Curie-like impurity ($C = 0.375$ $cm^3\ mol^{-1}$ K, $g = 2$) representing 2.8% of the Cu(II) ions in the material.

Three different magnetic interaction pathways can be imagined in **1**, e.g. bis(μ-*O*,*O′*-acetato), bis(μ-*O*-acetato), and bis(μ-methoxo) bridges (Cu−O−Cu angle of 102.4°). Through-space direct exchange couplings can be neglected because of the large Cu−Cu separations. Unfortunately, no theoretical model is available to account for the corresponding 2D magnetic interaction scheme. Nevertheless, as discussed above, the structure can indeed be described as a 2D array of rectangular tetranuclear units of a formal composition $[Cu_4(CH_3COO)_4(CH_3O)_4]$, being assembled by means of tetracoordinated acetate ions, as shown in Figure 1. Bis(μ-*O*-acetato) bridges were already shown to be negligible in polymeric chains, for which a dimeric model could be applied.[3] This is understandable from the configuration around the Cu(II) ions: on one side, the μ-*O*-acetato bridges in a loosely bonded axial position, where the spin density of the unpaired electron is expected to be very low (d_{z^2} orbital). The appropriate Hamiltonian describing the magnetic coupling scheme in a rectangular tetranuclear unit is then

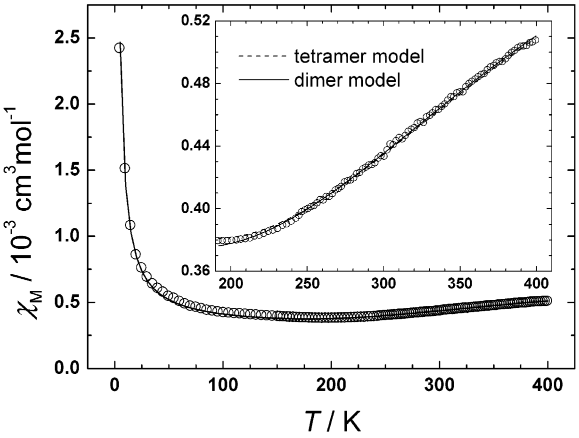

Figure 5. Magnetic susceptibility data/Cu(II) ion for $[Cu_2(MeO)_2(OAc)_2]$ in the range 5−400 K. The insert shows an enlargement of the high-temperature region ($T > 190$ K). The dashed line was calculated from a rectangular tetranuclear model with $J_1 = -409(2)$ cm^{-1} and $J_2 = -40$ to 0 cm^{-1}, while the full line corresponds to a dinuclear model with $J = -418(2)$ cm^{-1} (see text).

$$\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_{1a}\hat{S}_{2a}) - 2J_2(\hat{S}_1\hat{S}_{1a} + \hat{S}_2\hat{S}_{2a}) \qquad (1)$$

The resulting low-lying energy levels $E_1 = -(J_1 + J_2)$, $E_2 = J_1 - J_2$, $E_3 = J_2 - J_1$, $E_4 = J_1 + J_2$, $E_5 = J_1 + J_2 - 2(J_1^2 + J_2^2)^{1/2}$, and $E_6 = J_1 + J_2 + 2(J_1^2 + J_2^2)^{1/2}$ were deduced by an energy matrix diagonalization[22] and inserted into the van Vleck equation[23] to yield the following expression of the susceptibility/Cu:

$$\chi_{Cu} = [(N_A g^2 \mu_B^2)/4k_BT]\{[10\exp(-E_1/k_BT) + 2\exp(-E_2/k_BT) + 2\exp(-E_3/k_BT) + 2\exp(-E_4/k_BT)]/[5\exp(-E_1/k_BT) + 3\exp(-E_2/k_BT) + 3\exp(-E_3/k_BT) + 3\exp(-E_4/k_BT) + \exp(-E_5/k_BT) + \exp(-E_6/k_BT)]\} \qquad (2)$$

This expression, including terms for the paramagnetic impurity (3.8%) and the TIP (2.72×10^{-4} $cm^3\ mol^{-1}$), resulted, by minimizing the expression $R = \Sigma_i(\chi_{calcd} - \chi_{obs})^2/\Sigma_i(\chi_{obs})^2$ over the whole temperature range, in a range of similar fits (dashed line in Figure 5) corresponding to the parameters $J_1 = -409(2)$ cm^{-1}, $g = 2.20(3)$, and J_2 comprised between −40 and 0 cm^{-1}. This indicates that the interaction parameter J_2 is too small compared to J_1 to be accessed with accuracy. To confirm this further, the data were fit to a simpler dimer model,[24] which resulted (full lines in Figure 5) in the best-fit parameters $J = -418(2)$ cm^{-1} and $g = 2.30(3)$ (TIP = 3.0×10^{-4} $cm^3\ mol^{-1}$, paramagnetic impurity = 3.0%). The magnetic behavior of **1** is therefore dominated by a strong antiferromagnetic coupling within a Cu(II) pair. The measures of this coupling are comparable in both models employed (J_1 and J), as can be seen by the comparable agreement obtained with experimental data in the high-temperature region (insert in Figure 5). The overall

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quality of the fit obtained with the dimer model indicates that any other coupling pathway in **1** is, if significant, very small and is not necessary to reproduce the data. Interestingly, the value expected[25] for a planar symmetric bis(μ-alkoxo)-copper(II) dimeric unit with a Cu−O−Cu angle of 102° is close to that of J_1 or J (ca. 495 cm^{-1}). On the other hand, while tetrakis(μ-O,O'-carboxylato) bridges are extremely frequent in Cu(II) compounds and produce strong antiferromagnetic exchange coupling, bis(μ-O,O'-carboxylato) bridges are encountered only with Cu(I). The dominant strong antiferromagnetic exchange coupling can therefore be assigned to the bis(μ-methoxo) bridges. To the best of our knowledge, the bis(μ-O,O'-carboxylato) exchange pathway between Cu(II) ions had not been characterized so far. The extremely weak character, compared to that of tetrakis(μ-O,O'-carboxylato) bridge, of that coupling found here is surprising with respect to the known literature of tetrakis(μ-O,O'-carboxylato)-bridged Cu(II) compounds. It may arise though from the involvement of the $d_{x^2-y^2}$ magnetic orbital in the methoxo-bridge toward another Cu(II) ion.

In conclusion, although the compound described in this paper has been known for 100 years, its structure has just been clarified. Despite an apparent simplicity, this complex is shown to be an intricate 2D network, achieved by means of three different types of bridging anions: bis(μ-O,O'-acetato), bis(μ-methoxo), and bis(μ-O-acetato) bridges. The latter rare binding mode is unprecedented for Cu(II) complexes. Very strong antiferromagnetic exchange couplings realized via bis(μ-methoxo) bridges dominate the temperature dependence of the magnetic susceptibility of **1**, while the rare bis(μ-O,O'-carboxylato) bridge is shown to result in a weak, if significant, coupling.

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Supporting Information Available: X-ray crystallographic details for complex **1** in CIF format. This material is available free of charge via Internet at http://pubs.asc.org.

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