

SYNTHESIS AND CRYSTAL STRUCTURE OF BIS(ACETATO)BIS(2-METHYL-BENZIMIDAZOLE)COPPER(II)

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Abstract: The crystal structure of bis(acetato)bis(2-methylbenzimidazole)copper(II) has been determined. The complex is monoclinic, $P2_1/n$, with $a = 8.128(1) \text{ \AA}$, $b = 18.577(2) \text{ \AA}$, $c = 9.524(2) \text{ \AA}$ and $\beta = 94.92(2)^\circ$. The metal is six-coordinated forming with the ligands a slightly distorted octahedron. Eight water molecules were found in the crystal lattice.

Keywords: *one-dimensional, copper coordination complex, 2-methylbenzimidazole, hydrated copper acetate, hydrothermal reaction*

INTRODUCTION

Recently, a variety of coordination complexes with benzimidazole as a ligand have received considerable attraction due to their novel topology and interesting functions [1 - 3]. In particular, much attention has been paid to porous high-dimensional coordination complexes, because of their potential zeolite-like application [4 - 7]. For the preparation of this type of complexes, 1,3,5-benzenetricarboxylic acid (btcH_3) is widely employed because of its potential role as a multidimensional ligand [8 - 10]. For instance, Yaghi and co-workers reported the hydrothermal reaction between metal (II) acetate tetrahydrate, $[\text{M}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}]$; $\text{M} = \text{Co}, \text{Ni}$ or Zn], and btcH_3 to give 3-D coordination polymers of the $\text{M}_3(\text{btc})_2 \cdot 12\text{H}_2\text{O}$ type 3.

During the past years, several two and three-dimensional coordination complexes have been prepared from transition metal templates with mixed ligands of carboxylates and pyridyls, which can act as multidentate organic spacers. For example, a series of high-dimensional open frameworks were recently reported, in which the combinations of such organic spacers as btcH_3 , 1,4-benzenedicarboxylic acid, pyrazine, and 4,4'-bipyridine were utilized [11 - 13]. Recently, Min and co-workers [14] reported an one-dimensional copperpyridinedicarboxylate complex that contains square-planar $\text{Cu}(\text{II})$ centers exhibiting antiferromagnetic coupling. In this context, we set out to prepare copper coordination complexes from copper(II) acetate with 2-methylbenzimidazole as ligand by hydrothermal reaction. This gave an one-dimensional coordination complex with an empirical formula $[\text{Cu}(\text{AcO})_2(\text{Mebzm})_2 \cdot (\text{H}_2\text{O})_8]$ the structure of which was determined by using X-ray diffraction.

EXPERIMENTAL SECTION

Chemistry

In a round bottomed flask, the copper acetate monohydrate (3.00 g, 15.00 mmol) and 2-methylbenzimidazole (0.64 g, 5.00 mmol) were mixed in distilled water (15 mL). With constant stirring, the mixture was boiled under reflux 90 minutes and then cooled at room temperature. The blue bis(acetato)bis(2-methylbenzimidazole)copper(II) solid was collected by filtration, washed with distilled water, dried and recrystallized from EtOH-DMF (70/30) (yield: 40.1%, 1.16 g). Supplementary material was obtained from the aqueous filtrate after slow evaporation (2.89 g), total yield 65.3%. IR (KBr) ν 3325, 2805, 2675, 1580, 1462, 1425, 1300, 1243, 1050, 744, 712, 515 cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{38}\text{N}_4\text{O}_{12}\text{Cu}$: C 40.67, H 6.43, N 9.49. found: C 40.28, H 6.38, N 9.27.

X-Ray Diffraction

The crystal structure has been determined by single-crystal X-ray diffraction techniques and refined by full-matrix least-squares procedures. The data were collected on a CAD4 Enraf–Nonius [15] diffractometer with graphite monochromatized $\text{CuK}\alpha$ radiation. The cell parameters were determined by least-squares from the setting angles for 25 reflexions.

In the collection of intensities the $\theta/2\theta$ scan method was used, and 2790 independent reflexions were collected in the region $\theta < 65^\circ$. Correction was made for Lorentz and polarisation effects. 2060 reflexions with $I > 2\sigma(I)$ were considered observed and were used in the subsequent calculations. Semi-empirical method of absorption correction was applied. Full crystallographic results have been deposited at the Cambridge Crystallographic Data Centre (CCDC), UK, as Supplementary Materials [16]. The position of non-H atoms were determined by the program SHELXS 86 [17] and the position of the H atoms were deduced from coordinates of the non-H atoms and confirmed by Fourier synthesis. H atoms were included for structure factor calculations but not refined.

RESULTS AND DISCUSSION

Crystal data and experimental conditions are summarized in Table 1. The atomic and thermal parameters are contained in Table 2. Selected bond distances and angles are listed in Table 3. The hydrogen bonding geometry is given in Table 4.

Table 1. Crystal data and structure refinement for $[\text{Cu}(\text{AcO})_2(\text{Mebzm})_2(\text{H}_2\text{O})_8]$

Empirical formula	$\text{C}_{10}\text{H}_{19}\text{Cu}_{0.50}\text{N}_2\text{O}_6$
Formula weight	295.04
Temperature	296(2) K
Crystal system	monoclinic $Z = 4$
Space group	$P 2_1/n$
Unit cell dimensions	$a = 8.128(1) \text{ \AA}$ $b = 18.577(2) \text{ \AA}$ $c = 9.524(2) \text{ \AA}$ $\beta = 94.92(2)^\circ$
Calculated density	1.368 mg/m^3
Absorption coefficient	1.624 mm^{-1}
F(000)	622
Crystal size	$0.20 \times 0.20 \times 0.12 \text{ mm}^3$
Theta range	4.76 to 59.90°
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54178 \text{ \AA}$)
Reflections collected / unique	2060 / 2060
θ_{max}	59.90 97.0%
Goodness-of-fit on F^2	1.147
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0352$, $wR_2 = 0.0988$
$(\Delta/\sigma)_{\text{max}}$	0.025
$(\Delta/\sigma)_{\text{max}}$	0.311 \AA^{-3}
$(\Delta/\sigma)_{\text{max}}$	-0.276 \AA^{-3}

Table 2. Atomic coordinates and equivalent isotropic thermal parameters (U_{eq} (Å²))

	x	y	z	U_{eq}
C(1)	0.1811(3)	-0.0128(2)	-0.3957(3)	0.037(1)
C(2)	0.2363(4)	0.0216(2)	-0.5115(3)	0.052(1)
C(3)	0.2348(4)	0.0952(2)	-0.5105(3)	0.064(1)
C(4)	0.1785(4)	0.0337(2)	-0.3986(3)	0.060(1)
C(5)	0.1217(3)	0.0995(1)	-0.2826(3)	0.044(1)
C(6)	0.1245(3)	0.0254(1)	-0.2823(2)	0.032(1)
N(7)	0.0810(2)	-0.0246(1)	-0.1827(2)	0.031(1)
C(8)	0.1099(3)	-0.0890(1)	-0.2344(2)	0.035(1)
N(9)	0.1703(2)	-0.0841(1)	-0.3613(2)	0.040(1)
C(10)	0.0811(4)	-0.1588(2)	-0.1644(3)	0.054(1)
C(11)	0.4733(3)	0.0123(2)	0.1820(3)	0.059(1)
C(12)	0.3012(3)	0.0166(2)	0.1100(3)	0.039(1)
O(13)	0.2129(2)	-0.0394(1)	0.1047(2)	0.041(1)
O(14)	0.2493(2)	0.0741(1)	0.0563(2)	0.051(1)
O(15)	0.1987(3)	0.3018(1)	0.0161(2)	0.056(1)
O(16)	0.1738(3)	0.3244(1)	0.3120(2)	0.062(1)
O(17)	0.0635(3)	0.6934(1)	0.4816(3)	0.066(1)
O(18)	0.0506(3)	0.7304(1)	0.1859(3)	0.076(1)
Cu(19)	0.0	0.0	0.0	0.028(1)

Table 3. Relevant interatomic distances (Å) and angles (°)

C(12)-O(14)	1.241(3)	Cu(19)-O(14)	2.470(2)
C(12)-O(13)	1.264(3)	N(7)-Cu(19)-N(7, I)	180.00(15)
O(13)-Cu(19)	2.0564(17)	N(7)-Cu(19)-O(13)	90.83(7)
Cu(19)-O(13, I)	2.0564(17)	N(7, I)-Cu(19)-O(13)	89.17(7)
Cu(19)-N(7, I)	1.9658(18)	O(13)-Cu(19)-O(14)	56.82(7)

Table 4. Hydrogen-bonding geometry (Å, °)

O-H...A	O-A	O-H	O-H...A
O(15, I)-H(15A, I)...O(18, II)	2.738(3)	1.80(5)	171(4)
O(15, I)-H(15B, I)...O(17, III)	2.790(3)	1.92(5)	164(5)
O(16, I)-H(16A, I)...O(13, IV)	2.784(3)	1.92(3)	164(3)
O(16, I)-H(16B, I)...O(15, I)	2.873(3)	2.09(3)	150(3)
O(17, I)-H(17A, I)...O(14, IV)	2.730(3)	1.83(3)	175(3)
O(17, I)-H(17B, I)...O(16, V)	2.889(3)	1.97(3)	175(3)
O(18, I)-H(18A, I)...O(16, IV)	2.839(3)	1.96(3)	168(3)
O(18, I)-H(18B, I)...O(17, I)	2.892(4)	2.01(3)	164(3)

Symmetry Codes :

II (0.5-x, y-0.5, -0.5-z); III (0.5-x, y-0.5, 0.5-z); IV (0.5-x, 0.5+y, 0.5-z); V (-x, 1-y, 1-z).

Two 2-methylbenzimidazole and two acetate molecules are coordinated to each Cu atom, the two 2-methylbenzimidazole molecules via N(7), and the two acetate via the carboxylate O atoms. Each Cu atom is centro-symmetrically surrounded by these four ligands. The coordination around the Cu atom is planar for the four closest centrosymmetric ligand atoms, which nearly form a square. Both the second carboxylate O atoms interact weakly with the Cu (19) atom at 2.470(2) Å and, as a result the metal

is six-coordinated forming a slightly distorted octahedron [18]. The distortion is indicated by the angle value $\text{O13-Cu19-O14} = 56.82(7)^\circ$ (Figure 1).

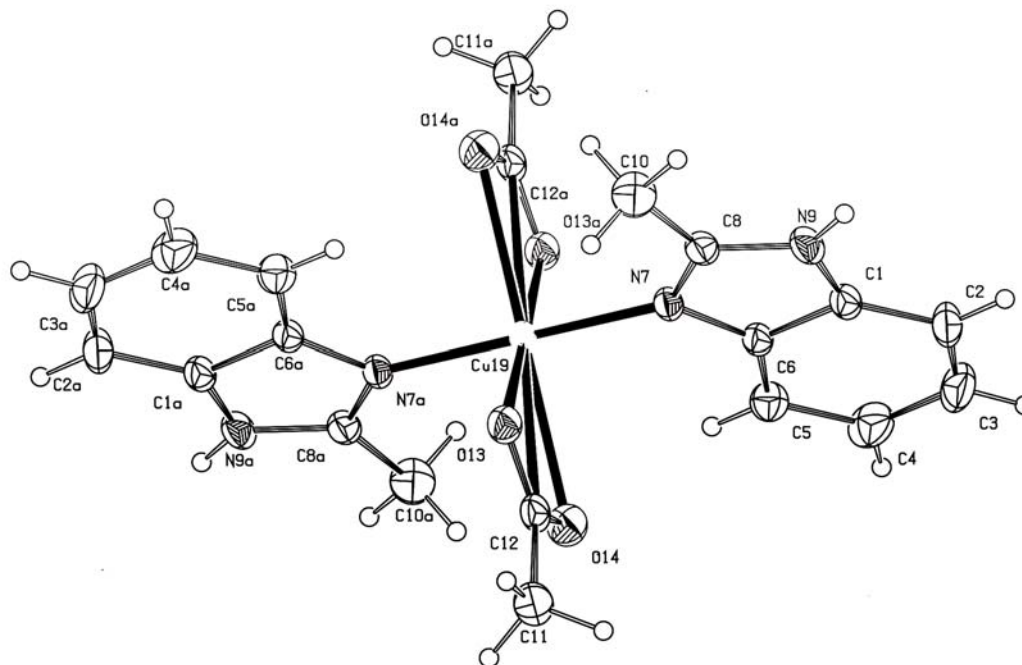


Figure 1. ORTEP drawing for $[\text{Cu}(\text{AcO})_2(\text{Mebzm})_2(\text{H}_2\text{O})_8]$ showing the atom-numbering scheme and 30% probability thermal ellipsoids, and H atoms are shown as spheres of arbitrary

The complex $[\text{Cu}(\text{AcO})_2(\text{Mebzm})_2(\text{H}_2\text{O})_8]$ is air-stable and is not soluble in common organic solvents. Its IR spectrum shows the asymmetric and symmetric carboxylate stretches: $3362, 3275, 1612, 1600, 525 \text{ cm}^{-1}$, while the band at 3325 cm^{-1} ascertains the presence of coordinated water molecules [19]. The band observed at 1410 cm^{-1} has been attributed to acetate groups. Furthermore, the presence of a peak around 515 cm^{-1} indicated Cu-O stretching vibrations [20]. The observed downfield shift of $\gamma_{\text{N}=\text{C}}$, going from free ligand with metal complex, suggests a neutral nitrogen (sp^2) pyridinic coordination of benzimidazolyl groups with the metal. The presence of water molecules in the crystal lattice was demonstrated by thermogravimetric analysis of the complex (loss of water at 175°C). On the other hand, the complex is stable up to 260°C without decomposition.

CONCLUSION

In conclusion, we have described the preparation and monoclinic crystal structure of bis(acetato)bis(2-methylbenzimidazole)copper(II). In the complex the Cu atom is square-planar coordinated by two acetate anions groups, and by two more distant monodentate 2-methyl-benzimidazole groups to complete the distorted octahedral coordination.

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