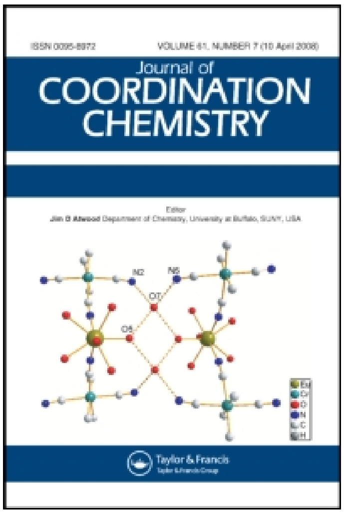

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Valach, F. , Grobelny, R. , Glowiak, T. , Mrozinski, J. , Lukeš, V. and Blahová, Z.(2010) 'Structural study of semi-coordination in a seven-coordinate copper(II) complex: distortion isomerism of [Cu(CH_3COO)$_2$(4-aminopyridine)$_2$(H_2O)]', Journal of Coordination Chemistry, 63: 10, 1645 — 1651, First published on: 11 June 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958972.2010.489204
URL: http://dx.doi.org/10.1080/00958972.2010.489204

Journal of Coordination Chemistry
Vol. 63, No. 10, 20 May 2010, 1645–1651

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Structural study of semi-coordination in a seven-coordinate copper(II) complex: distortion isomerism of $[Cu(CH_3COO)_2(4\text{-aminopyridine})_2(H_2O)]$

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(*Received 8 July 2009; in final form 19 February 2010*)

[Di(acetato)bis(4-aminopyridine)aquacopper(II)] exists in two different monoclinic forms. The crystal structure of Form **1**, which crystallizes in space group $P2_1/c$, was determined by X-ray crystallography. Experimental data was then compared with that found for Form **2**, which crystallizes in space group $C2/c$. The seven-coordinate environment of copper in both forms is consistent with the bond-valence model. The asymmetric copper(II) coordination of Form **1** is consistent with the density-functional theory. The isomers differ in distortion of the pentagonal bipyramid as the coordination polyhedron around Cu. Carboxylate groups for both isomers are bonded to copper as bidentate ligands. The Cu in Form **1** is semi-coordinated by two long carboxylate O bonds to create the seven-coordinate environment (Cu $\cdots$ O distances are 2.785(4) and 2.9996(5) Å). Infrared and electron spin resonance spectra of both isomers are consistent with their crystal structures.

Keywords: Copper(II); Carboxylate; 4-Aminopyridine; Distortion isomers

1. Introduction

Copper(II) complexes have distortion isomers [1, 2] which differ in the distortion of the coordination polyhedron around copper. The relationship between plasticity of the coordination sphere and the distortion isomerism of six-coordinate copper(II) complexes was studied [3]. The plastic features of the Cu(II) coordination sphere are manifested in mutual dependence of the distances between copper and the ligand, weakening of the bonds on one axis causes strengthening of the bonds on the remaining axis and *vice versa*. Another approach showed the importance of the electronic interaction of ligands for the tetragonal distortions of $[CuX_6]^{4-}$ $(X = F, Cl)$ [4].

Carboxylate groups are relatively rigid in contrast to the inner coordination sphere of Cu(II) complexes. Recent studies of six-coordinate copper(II) complexes showed a continuous transition between bidentate and monodentate bonding of carboxylate with

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.489204

many intermediate states [5]. Changes in interatomic Cu–O distances are much more sensitive for this transition than the O–Cu–O angle [6, 7]. Recently, we reported the crystal structure for blue [Cu(CH_3COO)$_2$(4-aminopyridine)$_2$(H_2O)] crystals that crystallize in the $C2/c$ (No. 15) monoclinic space group [8] (Form **2**). For Cu $\cdots$ N, O connections, these semi-coordinated bonds are longer than normal bonds, but shorter than van der Waals contacts. The principles of the bond-valence model [9] allow a more precise estimation of the upper limits of semi-coordinated Cu $\cdots$ O, N bond lengths, regardless of the oxidation state of copper [10]. As part of our investigation of seven-coordinate copper(II) carboxylates, we report on the crystal structure of Form **1** of the title compound.

2. Experimental

2.1. *Preparation of the complex*

Form **1** of [Cu(CH_3COO)$_2$(4-aminopyridine)$_2$(H_2O)] was prepared using the same procedure as for Form **2** [8] except that the copper(II) solution was stirred at room temperature. Analysis for Cu(CH_3COO)$_2$(4-aminopyridine)$_2$(H_2O) (%): Cu, 16.38; C, 43.35; H, 5.20; and N, 14.44. Found (%): Cu, 16.17; C, 44.12; H, 5.42; and N, 14.31.

2.2. *Crystallography*

An almost needle-shaped crystal (0.15 × 0.15 × 0.25 mm) of Form **1** was scanned on a Kuma KM-4 diffractometer at 293 K with Cu radiation, $\lambda = 1.54180$ Å. This compound was crystallized in the space group $P2_1/c$ (No. 14) with lattice parameters $a = 11.883(2)$ Å, $b = 6.728(1)$ Å, $c = 21.191(7)$ Å, $\beta = 96.68(3)^\circ$, and $V = 1682.7(5)$ Å^3. The calculated density was $Z = 4$, $D_x = 1.531\ \mathrm{g\,cm^{-3}}$ and 13,189 independent reflections were measured with $R_{int} = 0.032$. These calculations were made by programs within the Kuma KM4's software ($\mu = 2.1\ \mathrm{mm^{-1}}$).

The structure was solved *via* direct methods using the SHELXS-97 program [11]. The parameters of the structure were refined on F^2 using full-matrix, least-squares *via* SHELXL-97 [11] (298 parameters). The final results were $R = 0.032$ and $R_w = 0.093$ for 3113 observed data points. The figures were prepared by the ORTEP-3 program for Windows [12] (Supplementary material).

2.3. *Spectral measurements*

Diffuse reflectance electronic spectra of both isomers were recorded for solid powdered samples from 350 to 1000 nm using a Beckman UV 5240 spectrometer with a special attachment ($BaSO_4$ as reference). Infrared (IR) spectra were measured in KBr pellets as Nujol mulls on a Perkin Elmer 180 spectrometer from 100 to 4000 cm^{-1}. All of these measurements were done at room temperature. Electron spin resonance (ESR) powder spectra were measured at 298 and 77 K using an ESP 300E Bruker spectrometer with bands X9.745707GH and 9.426870GH.

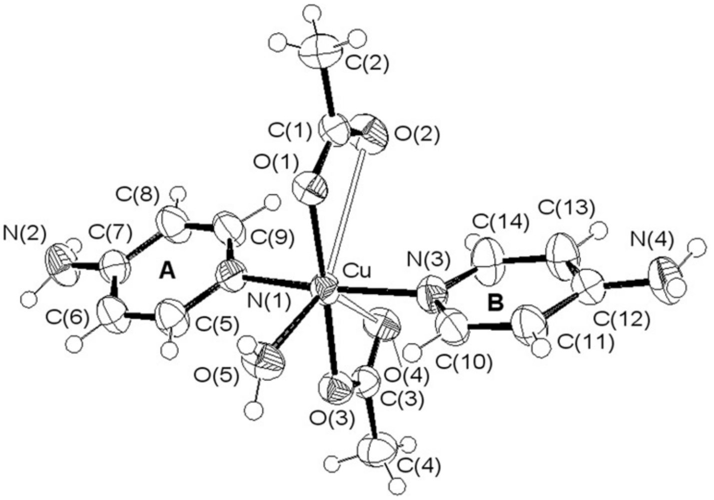

Figure 1. Molecular structure of Form **1** of [Cu(CH_3COO)$_2$(4-aminopyridine)$_2$(H_2O)] showing atom numbering of the asymmetric unit. Semi-coordinated Cu···O bonds are shown by the white cones.

2.4. *Quantum chemical calculations*

The electronic ground state geometries of the system (figure 1) were optimized using density-functional theory (DFT) [13]. In comparison with the semi-empirical quantum chemical treatments, the DFT method does not require the special parametrization or the setting of additional parameters in the Hamiltonian for the reliable description of physical properties. In our calculations, we selected Becke's hybrid functional using Lee, Yang and Parr's correlation functional (B3LYP), which gives reliable results for a majority of organic and inorganic compounds [14, 15]. The optimal geometries obtained were confirmed to be real minima *via* a frequency calculation (no imaginary frequencies). All calculations were performed using Gaussian 03 [15]. The 6-31G(d) basis set for Cu and 6-31 + G(d, p) basis sets for the C, N, O, and H atoms [16] were used.

3. Results and discussion

The crystal structure of both isomers consists of [Cu(CH_3COO)$_2$(4-aminopyridine)$_2$(H_2O)$_2$] complex units mutually bonded by hydrogen bonds. An ORTEP diagram of Form **1** appears in figure 1. Selected bond lengths and angles are given in table 1. Hydrogen bond lengths and bond angles for Form **1** are given in table 2.

For both isomers, the copper–oxygen distances are less than 3.07 Å [10], which implies bidentate bonding of carboxylate to copper. The Cu–O(4) bond of Form **1** is longer than the typical Cu(II)–O bond lengths (2.3(2) Å) for chelated acetates [17]. The length of the Cu(II)–O(4) bond was calculated using the bond-valence method [9, 18, 19]. Predicted Cu(II)–O(4) bond length is 2.859(2) Å, which is slightly longer than

Table 1. Selected bond distances (Å) and angles (°) for Form **1** of [$Cu(CH_3COO)_2$ (4-aminopyridine)$_2$(H_2O)] with estimated standard deviations (ESDs) in parentheses.

Cu–N(1)	2.002(5)	N(1)–Cu–O(1)	90.37(2)
Cu–N(3)	2.006(5)	N(3)–Cu–O(1)	90.02(1)
Cu–O(1)	1.976(6)	N(3)–Cu–O(3)	90.49(2)
Cu···O(2)	2.9996(5)	O(1)–Cu–O(5)	91.35(1)
Cu–O(3)	1.974(6)	O(1)–Cu···O(4)	132.20(2)
Cu···O(4)	2.785(1)	O(1)–Cu···O(2)	47.34(1)
Cu–O(5)	2.482(5)	O(3)–Cu···O(4)	51.85(1)
C(1)–O(1)	1.274(2)	O(1)–C(1)–O(2)	123.65(1)
C(1)–O(2)	1.229(2)	O(1)–C(1)–C(2)	116.40(1)
C(1)–C(2)	1.506(4)	C(2)–C(1)–O(2)	119.94(1)
C(3)–O(3)	1.271(2)	O(3)–C(3)–O(4)	123.11(1)
C(3)–O(4)	1.236(2)	O(3)–C(3)–C(4)	116.01(1)
C(3)–C(4)	1.504(4)	C(4)–C(3)–O(4)	120.87(1)

Table 2. Lengths (Å) and angles (°) of hydrogen bonds for Form **1** of [$Cu(CH_3COO)_2$ (4-aminopyridine)$_2$(H_2O)] with ESDs in parentheses.

D–H	A	H···A	D···A	D–H···A
O(5)–H(2)	O(4^a)	2.12(3)	2.957(2)	167(3)
O(5)–H(1)	O(2^a)	1.98(3)	2.805(2)	172(3)
N(2)–H(12)	O(4^b)	1.96(3)	2.902(2)	177(3)
N(2)–H(11)	O(3^c)	2.33(3)	3.082(2)	145(3)
N(4)–H(17)	O(2^d)	2.06(3)	2.916(2)	162(3)
N(4)–H(18)	O(1^e)	2.04(3)	2.930(2)	171(2)

Symmetry code: $^a x, y-1, z$; $^b -x, y-½, ½-z$; $^c -x, y+½, ½-z$; $^d -x, y+½, ½-z$; $^e -x, y+½, ½-z$.

the observed value of 2.784(5) Å. Such a difference can be caused by hypervalence of copper. The bond-valence sum around the seven-coordinate copper is 2.014(1). The Mulliken charge for Cu is 0.017 v.u.

Selected geometrical parameters of both isomers are compared with the DFT results in table 3. The length of Cu–O(5) bond and the O(4)···Cu–O(5) angle as found *via* DFT is 4.016 Å and 38.49°, respectively. Observed values are 2.482(5) Å and 43.58(1)° for Form **1** and 2.307(2) Å and 46.47(5)° for Form **2**, respectively. Such a large difference with respect to observed values can be explained by stabilization of Cu–O (water) bonds in the crystal structures of both isomers by intermolecular hydrogen bonds connecting [$Cu(CH_3COO)_2$(4-aminopyridine)$_2$(H_2O)$_2$] with adjacent units. Due to computing limitations, the hydrogen bonded atoms of adjacent units were not involved in the DFT calculations. The hydrogen bonds O(5)–H(2)···O(4) and O(5)–H(1)···O(2) connect the units into infinite 2-D chains along direction **b** of the unit cell (figure 2). Cu···O(2), O(4) distances for Form **1** are very close to those obtained *via* DFT calculations (table 3). The parameters calculated by DFT starting from the ground state geometry of Form **2** do not differ significantly from those calculated using the geometry of Form **1**. The bond valences (bond strengths) of the shorter Cu–O(1) and O(3) bonds are 0.425(6) and 0.427(6), respectively. However, the valences of Cu···O(2) and O(4) contacts are 0.0458(2) and 0.01014(7), respectively which indicate very weak bonds. The carboxylic O(2) and O(4) atoms are

Table 3. Comparison of selected geometrical parameters for isomers of [$Cu(CH_3COO)_2$ (4-aminopyridine)$_2$(H_2O)] along with DFT calculation results. ESDs are in parentheses. Maximum of deviations from the mean are noted ±.

Parameter	**1**	**2**	DFT
Mean Cu–N	2.004 ± 0.002	2.007(2)	2.036 ± 0.003
Mean Cu–O(1),O(3)	1.975 ± 0.001	1.9592(6)	1.97 ± 0.02
Cu···O(2)	2.9996(5)	3.041(1)	3.050
Cu···O(4)	2.785(1)	3.041(1)	2.794
O(1)–Cu–O(3)	175.95(3)	176.60(3)	154.57
N(1)–Cu–N(3)	170.02(2)	165.38(3)	166.05
Mean O–Cu···O	50 ± 2	46.47(5)	50 ± 3
Mean Cu–O–C	115 ± 4	120.1(1)	115 ± 5
Mean Cu–O–C–C	1.1 ± 0.4	3.4(2)	3 ± 1
Mean Cu–O–C–O	1.6 ± 0.6	1.01(4)	0 ± 3

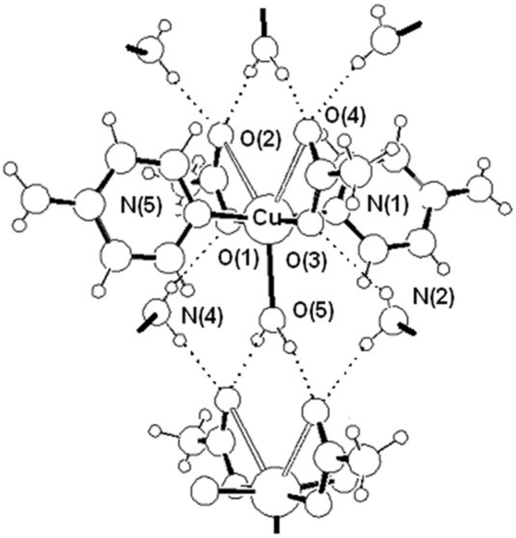

Figure 2. Hydrogen bonds of Form **1**.

semi-coordinated to copper. The coordination polyhedron around copper of Form **1** is a deformed pentagonal bipyramid and the equatorial plane of the bipyramid is formed by oxygen of both carboxylates and water (figure 1). Maximum deviation from planarity is 0.0558(2) Å for O(1). The copper deviates from the least-squares plane of the oxygens by 0.092(3) Å toward N(1), and slightly deviates from the least-squares plane as defined by the O(1), O(3), N(1), and N(3) toward O(5) atom by 0.0522(3) Å. The position of acetate bonded *via* Cu–O(3) is stabilized by the longer Cu···O(4) bond. A slightly greater value of the O(2)–C(1)–O(1)–Cu (2.13(4)°) torsion angle as compared to the O(4)–C(3)–O(3)–Cu (1.01(4)°) indicates significant stabilizing effect that the weak Cu···O(2) bond has at a distance 2.9996(5) Å, close to 3.041(1) Å as found for Form **2** (table 3). However, the Cu···O(4) bond is much shorter than the weak Cu···O bonds of Form **2**. The mean lengths of N–C and C–C bonds of the 4-aminopyridine of Form **1** do not significantly deviate from those found in the crystal structure of 4-aminopyridine [20]. The dihedral angle created by the least-squares planes of 4-aminopyridines **A** and **B** (figure 1) is 16.75(1)°. This value is very close to the 16.89° obtained *via* DFT calculations. Molecule **B** is almost parallel to the Cu–O(5) vector. The angle between the normal- to least-squares plane of 4-aminopyridyne **B** and the Cu–O(5) vector is 89.40(2)°. The same type of angle as created by 4-aminopyridyne **A** is 72.83(2)°. Both angles differ from the values of 64.02(1)° found in the structure of Form **2**. $[Cu(CH_3COO)_2(4\text{-aminopyridine})_2(H_2O)_2]$ in crystals of both isomers are connected *via* hydrogen bonds into infinite 2-D chains along the Cu–O(water) direction (figure 2). Each carboxylic O is bonded by one hydrogen bond to water of the adjacent complex unit. The chains of Form **2** keep the twofold axes passing Cu–O(water) bonds. The chains of Form **1** keep such axes only approximately. The hydrogen bonds between the carboxylic O and amino groups of 4-aminopyridine of both isomers connect the chains into a 3-D network. The bond angles O(1)–Cu–O(3) of both isomers show a large difference with the value calculated by DFT. This angle is probably influenced by hydrogen bonds N(4)–H(18)$\cdots$O(1) and N(2)–H(11)$\cdots$O(3) (figure 2).

Electronic reflectance spectra of both isomers are similar, showing a broad asymmetric absorption centered at 17,200 and 17,050 cm^{-1} for Forms **1** and **2**, respectively. IR spectra for both isomers are very similar. In the region above 3000 cm^{-1}, they show the three bands expected for stretching of $-NH_2$ groups ($\nu = 3350$ and 3460 cm^{-1}) and water ($\nu = 3200\,cm^{-1}$). The acetate anti-symmetric $\nu_{as(COO)}$ and symmetric $\nu_{s(COO)}$ carboxylate vibrations for both isomers are at 1590 and 1408 cm^{-1}, respectively. The difference in the values of 182 cm^{-1} is relatively high, consistent with the external asymmetry of the carboxylate as bidentate ligands [21]. Strong bands at 310 and 265 cm^{-1} may be assigned to ν(Cu–O) and the band at 205 cm^{-1} to ν(Cu–N). ESR spectra of both isomers show only very small differences. At room temperature, the values for $g_\perp$ and $g_\parallel$ are 2.063 and 2.264, respectively (Form **1**), and 2.064 and 2.271, respectively (Form **2**). At 77 K, the values for $g_\perp$ and $g_\parallel$ are 2.067 and 2.284, respectively (Form **1**), and 2.065 and 2.264, respectively (Form **2**).

4. Conclusions

An isomer of the acetate of copper(II) complex with 4-aminopyridine, which crystallizes in the space group $P2_1/c$ (Form **1**), has been prepared and characterized. The crystal structures of Form **1** and the isomer which crystallizes in space group $C2/c$ (Form **2**) differ in the deformations of the coordination polyhedron around Cu(II). The bipyramid of Form **1** is asymmetric, while the bipyramid of Form **2** keeps C_2 symmetry with twofold axes passing the Cu–O(water) bond. Both forms are distortion isomers, which prevail in the chemistry of copper(II) complexes [1, 2]. According to the proposed notation [8], the copper coordination number for both isomers is $4+1+2$, $CuO_2N_2O'O_2''$.

Supplementary material

Bond-valence interpretation of the structural correlation for (RCOO)Cu fragments. The Crystallographic Information Files (CIF) have been deposited at the Cambridge

Crystallographic Data Centre under deposit numbers CCDC 714945 (Form **1**) and CCDC 747021 (Form **2**).

Acknowledgments

This work was sponsored by the grants 1/3572/06 and 1/0018/09 from the Slovak Grant Agency for Science (VEGA).

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