Synthesis, X-ray structural and thermal analysis of a novel copper compound containing dissymmetric independent 5- and 6-coordinate $CuL(H_2O)_n$ (n=2,3) units and hydrogen bond bridges

Duygu Barut[a], Neslihan Korkmaz[b], Stephen T. Astley[b,*], Muhittin Aygün [a,*]

[a] *Department of Physics, Faculty of Science, Dokuz Eylül University, 35160-Buca, İzmir, Turkey*

[b] *Department of Chemistry, Faculty of Science, Ege University, 35100-Bornova, İzmir, Turkey*

E-mail addresses: stephen.thomas.astley@ege.edu.tr (S.T.Astley), muhittin.aygun@deu.edu.tr (M.Aygün)

Abstract

The synthesis, thermogravimetric and X-ray structure analysis of a highly unusual copper compound prepared from a chiral tridentate Schiff base ligand is reported. The title compound $[CuC_{16}H_{19}NO_7][CuC_{16}H_{17}NO_6].H_2O$ crystallizes in the orthorhombic crystal system in space group $P2_12_12_1$ with Z = 4. Two independent $CuL(H_2O)_x$ complexes are present in the same unit cell, one five- and the other six- coordinate. The five-coordinate copper(II) centre occupies a distorted square-pyramidal geometry whereas the six-coordinate copper(II) centre has a distorted octahedral geometry. The independent copper complexes and the uncoordinated water molecule are joined together with intermolecular hydrogen bonds in a two-dimensional supramolecular network which lies parallel to the ab plane.

Keywords: Schiff base Cu(II) complex; Crystal structure; Thermal analysis; 2D supramolecular structure

1. Introduction

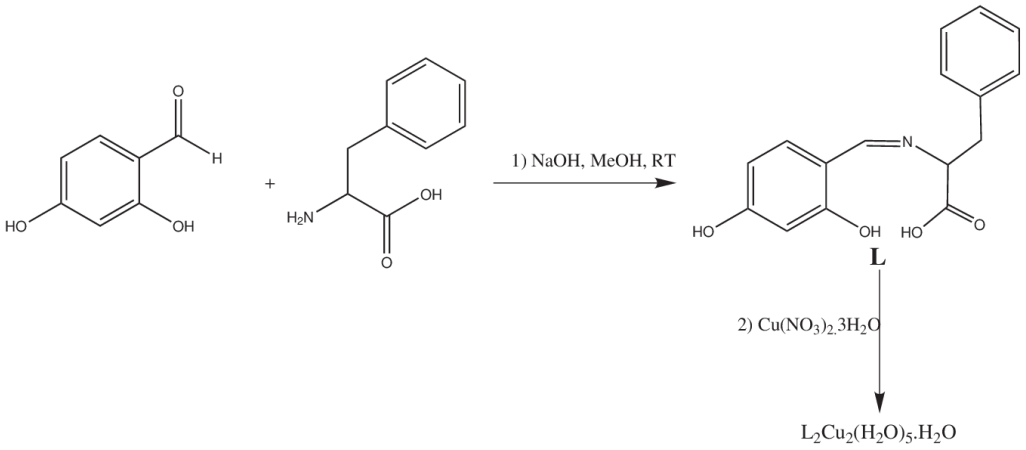
Copper complexes of tridentate Schiff base ligands derived from amino acids and aromatic aldehydes have received considerable attention as a result of their inherent catalytic,[1-3] and biological activity and their potential similarity to enzymes.[4-12] Although different structures are often adopted, it can reasonably be assumed that these properties are partly due to the availability of sites of coordinative unsaturation at the metal centre and the presence of amino acid residues. In particular a defining property of Cu(II) ions is that, unless a tridentate ligand is flexible enough to complement its distorted coordination sphere,[13] Cu(II) will preferably bind only one ligand.[14] Thus, for copper (II) complexes containing only solvent molecules in addition to a tridentate ONO Schiff base ligand, although a 4-coordinate square planar geometry is possible,[15] in the majority of cases the Cu(II) ion adopts a 5-coordinate square pyramidal geometry where the fourth and fifth coordination sites are occupied by solvent or bridging ligands. These structural constraints allow the formation of mononuclear,[16-18] oligonuclear,[19-21] or polymeric structures.[22] Similar observations have been made for related complexes containing an additional ligand instead of a coordinated solvent molecule,[23-24] and for reduced Schiff base ligands.[14] Therefore, we were interested and surprised to discover that copper (II) complexation of a tridentate Schiff base ligand (L) derived from phenylalanine and 2,4-dihydroxybenzaldehyde resulted in a structure that contains two independent $Cu(II)L(H_2O)_x$ units. In

one independent unit, the Cu(II) centre adopts the expected square pyramidal geometry. However, in the second independent unit, an additional water molecule has coordinated to afford an octahedral geometry. Although a square pyramidal/octahedral arrangement has previously been observed with the highly flexible dipicolylamine ligand,[25] this example is perhaps more striking as the different geometries are created just by a differing degree of solvent associaton. We consider this to be a clear demonstration of the versatility of Cu(II) and its ability to coordinate and uncoordinate solvent or substrate molecules which is believed to be a fundamental and necessary property of copper-based enzymes.[12]

2. Experimental

2.1. Synthesis of the title Complex

To a solution of D-Phenylalanine (1.0 mmol, 165.2 mg) in 5 ml methanol, NaOH (1.0 mmol, 40 mg) in 3 ml methanol was added. Then, 2,4 dihydroxybenzaldehyde (1.0 mmol, 138 mg) was added and the reaction mixture was stirred at room temperature for 2 h. The reaction was monitored by TLC and a bright yellow solution was obtained. After the complete consumption of the starting materials, $Cu(NO_3)_2.3H_2O$ (1.0 mmol, 241.6 mg) in 5 ml methanol was added dropwise to the reaction flask. Stirring was continued overnight to afford a dark green solution. After monitoring by TLC, the solvent was removed. Bright green crystals were obtained after crystallization from MeOH by addition of a small amount of water. (0.23g, 58 %). Anal. Calc. for (%) $C_{32}H_{38}Cu_2N_2O_{14}$ ($L_2Cu_2(H_2O)_6$) (801.7 g/mol): C, 47.94; H, 4.78 N, 3.49; Found: C, 47.04; H, 4.45; N, 3.55. IR: KBr, 3367.8, 3085.6, 2912.1, 1606.6, 1548.1, 1495.9, 1450.5, 1353.8, 1289.2, 1226.8, 1122.9, 991.0, 706.6 cm^{-1} (Schem 1).



Scheme 1. The synthetic method for the preparation of $CuL(H_2O)_n$ (n=2,3).H_2O

2.2. X-ray Structure Determination

Intensity datasets were collected from the selected crystal at room conditions using an Agilent Diffraction Xcalibur diffractometer equipped with an Eos-CCD detector, operated at 50 kV and 40 mA, with Mo-Kα (λ = 0.71073 Å) radiation and a graphite monochromator. Data were absorption-corrected within the CrysAlis program.[26] Using Olex2,[27] the structure was solved with the SHELXS structure solution program using the Patterson Method and refined with the SHELXL refinement package using least squares minimization.[28] All non-H atoms were refined anisotropically. A summary of crystallographic data, experimental details, and refinement results for the complex are given in Table 1.

Table 1. Crystal data and structural refinement parameters

Crystal Data	
Empirical Formula	$[CuC_{16}H_{19}NO_7][CuC_{16}H_{17}NO_6].H_2O$
Formula Weight	801.72
Cell setting / Space group	Orthorhombic / $P2_12_12_1$
Unit cell dimensions	
	a = 9.0840 (6) Å
	b = 10.9080 (5) Å
	c = 35.416 (2) Å
Unit cell volume	3509.3 (3) $Å^3$
Temperature (K)	293
Absorption coefficient	1.282 mm^{-1}
Z / Density [g/cm^3]	4 / 1.52
F(000)	1656
Crystal size (mm^3)	0.6 x 0.2 x 0.1
θ range (°)	2.96 - 26.37
h range	$-11 \rightarrow 6$
k range	$-13 \rightarrow 7$
l range	$-43 \rightarrow 43$
Reflections collected / unique	9036 / 6069
Completeness to θ_{max}	98.86 %
Goodness-of-fit on F^2	1.184
Final R indices [$I > 2\sigma(I)$]	R1 = 0.066 , wR2 = 0.112
R indices all data	R1 = 0.084 , wR2 = 0.123
Large diff. peak and hole	0.44 / -0.58

3. Results and Discussions

3.1 Crystal Structure

The asymmetric unit of the complex consists of three independent molecules; a six-coordinate copper complex, a five-coordinate copper complex, and an uncoordinated water molecule. Fig.1 shows an ORTEP plot of the asymmetric unit.[29]

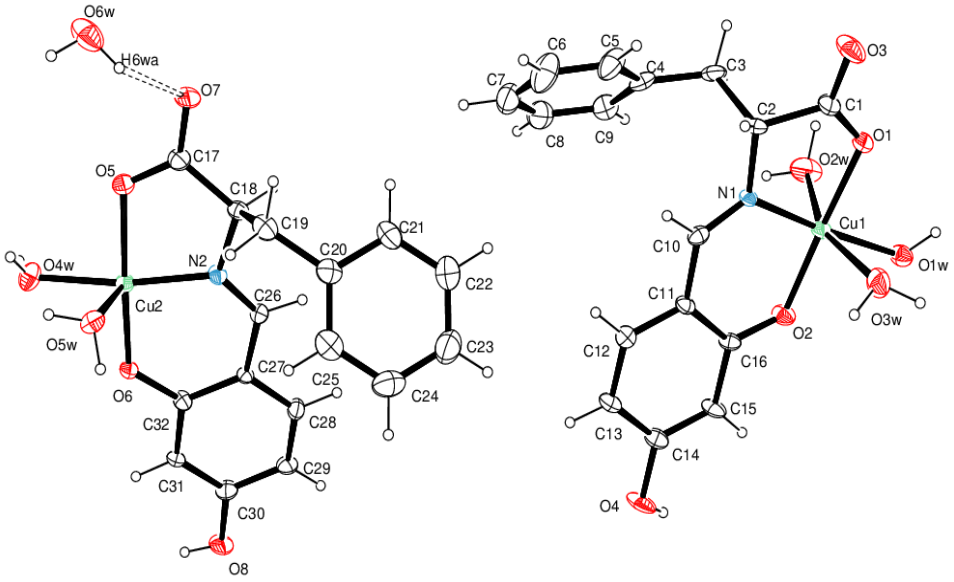


Fig 1. The molecular structure of the title compound in the asymmetric unit, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed line indicates the inter-molecular hydrogen bond.

In the six-coordinate copper(II) complex, the equatorial plane of the metal is occupied by the chelating tridentate (N1,O1,O2) ligand atoms and one oxygen atom (O1w) of a water molecule, while two water molecules (O2w,O3w) are in the axial positions. The Cu1 ion strays from the equatorial plane with a deviation of 0.057 (2) Å towards the O atom of the more strongly bound axial water molecule (O2w). As expected, due to the Jahn-Teller effect,[30-31] Cu-O distances in the axial directions [Cu1-O2w = 2.473 (6) Å, Cu1-O3w = 2.593 (6) Å] are longer than those in the equatorial plane. Although there is a small difference between these two bond lengths, these observations clearly suggest the geometry is best described as distorted octahedral. A comparison with literature data clearly indicates both of the water molecules are coordinated.[32-33] In the five-coordinate copper(II) complex, the geometry around the Cu2 atom is a distorted square-pyramidal. A nitrogen atom (N2), a phenolate oxygen atom (O6) and a carboxylate oxygen atom (O5) along with a coordinated water molecule (O4w) complete the basal plane. A second water molecule (O5w) is coordinated in the apical position. This apical Cu-O bond length [Cu2-O5w = 2.320(4) Å] is significantly shorter than the axial Cu-O distances observed in the octahedral unit. In this case, the Cu2 ion was found to stray from the basal plane with a deviation of 0.117 (2) Å towards the axial O5w.

A comparison of the two independent units indicated that most bond lengths were extremely similar (Table 2) and are entirely consistent with those observed in the literature.[34-36] The benzylic phenyl groups are not quite parallel to the planar ONO backbone of the ligand. The dihedral angles between the five-membered chelate rings and the phenyl rings in are 42.06 (3)° for Cu1 and 26.88 (2)° for Cu2, respectively. The two five-membered chelate rings are in the envelope conformation, i.e. the C2 atom is deviated from the plane by 0.064 (4) Å. The relative configuration at the C2 and C18 chiral centers are confirmed to be (R,R).

Table 2.Bond lengths (Å) and angles (°) for the compound

Distance (Å)			
Cu1-N1	1.915 (5)	Cu2-N2	1.913 (5)
Cu1-O1	1.963 (4)	Cu2-O5	1.961 (4)
Cu1-O2	1.892 (4)	Cu2-O6	1.898 (4)
Cu1-O1w	2.008 (4)	Cu2-O4w	1.983 (5)
Cu1-O2w	2.473 (6)	Cu2-O5w	2.320 (4)
Cu1-O3w	2.593 (6)	O5-C17	1.270 (7)
O1-C1	1.245 (7)	C32-O6	1.344 (6)
C16-O2	1.317 (7)		
Angle (°)			
O1-Cu1-N1	83.8 (2)	O1-Cu1-O2	174.4 (3)
O1-Cu1-O1w	90.7 (2)	O1-Cu1-O2w	86.8 (2)
O1-Cu1-O3w	82.1 (2)	O2-Cu1-N1	94.9 (2)
O2-Cu1-O1w	90.3 (2)	O2-Cu1-O2w	98.8 (2)
O2-Cu1-O3w	92.5 (2)	O1w-Cu1-N1	173.9 (2)
O1w-Cu1-O2w	79.0 (2)	O1w-Cu1-O3w	85.9 (2)
O2w-Cu1-N1	103.3 (2)	O2w-Cu1-O3w	161.2 (2)
O3w-Cu1-N1	90.6 (2)	O5-Cu2-N2	83.8 (2)
O5-Cu2-O6	170.6 (2)	O5-Cu2-O4w	89.9 (2)
O5-Cu2-O5w	88.4 (2)	O6-Cu2-N2	95.0 (2)
O6-Cu2-O4w	90.1 (2)	O6-Cu2-O5w	100.9 (2)
O4w-Cu2-N2	170.2 (2)	O4w-Cu2-O5w	87.0 (2)
O5w-Cu2-N2	100.3 (2)		

There are several intra and intermolecular hydrogen bonds and short atomic contacts which are responsible for the 2D supramolecular character of the structure as can be seen in Table 3. Both complexes form a one-dimensional infinite chain via O4-H4...O3 and O8-H8A…O7 hydrogen bonds along the b axis (Fig.2a,2b). In the asymmetric unit (x, 1+y, z), the cutoff distances are 1.85 Å for H4...O3 and 1.92 Å for H8A…O7. These distances are considerably shorter than the van der Waals atomic radii (2.72 Å) given by Bondi and Pauling.[37-38] Fig.2c displays additional intermoleculer O-H…O hydrogen bonding interactions which link

the two independent copper complexes forming a chain along the a axis (Table 3, entries 2, 5, 6, 7, 9, 11 and 12). As a result, the two independent copper complexes and the uncoordinated water molecule are joined together in a two-dimensional supramolecular network which lies parallel to the ab plane. This plane and the packing of the complexes can be seen in Fig.3.

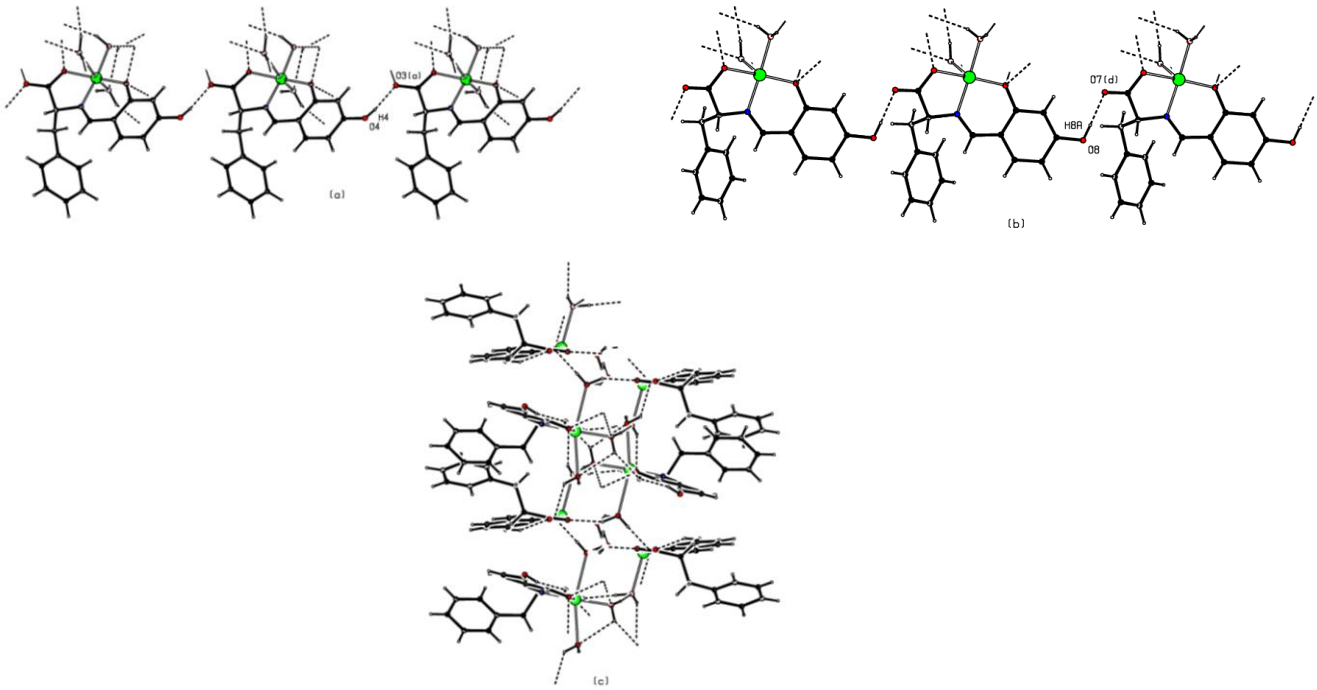


Fig 2. In the crystal structure, intermolecular O-H…O hydrogen bonds: **(a)** and **(b)** link the molecules into infinite chains along the b axis and **(c)** link the two molecules into infinite chains along the a axis (see **Table 3** for further details).

Table 3. Hydrogen-bond geometry (Å, °)

Bond	**D – H**	**H…A**	**D…A**	**D – H…A**
O4-H4…O3[a]	0.82	1.85	2.654 (8)	165
O1w-H1wA…O5w[b]	0.89	2.12	2.971 (6)	161
O1w-H1wB…O3[b]	0.89	2.18	2.968 (7)	147
O2w-H2wA...O6w	0.91	1.92	2.812 (8)	166
O2w-H2wB...O6[a]	0.91	2.10	2.841 (7)	138
O3w-H3wB...O6[c]	0.90	1.97	2.869 (7)	175
O3w-H3wA...O5[b]	0.90	1.96	2.759 (6)	147
O8-H8A...O7[d]	0.82	1.92	2.694 (7)	157
O4w-H4wA...O3w[f]	0.79	2.26	2.942 (8)	145
O4w-H4wB...O6w[e]	0.77	2.07	2.830 (9)	170
O5w–H5wB…O1[f]	0.87	1.85	2.717 (6)	173
O5w-H5wA...O2[d]	0.88	2.12	2.827 (7)	137
O6w-H6wA...O7	0.85	2.17	2.844 (8)	136
O6w-H6wB...O1w[f]	0.85	2.46	2.962 (8)	119
O6w-H6wB...O2[f]	0.85	2.16	2.990 (8)	167

Symmetry codes: (a): x,1+y,z ; (b): 1-x,1/2+y,1/2-z ; (c): 1+x,1+y,z ; (d): x,-1+y,z
(e): -x,-1/2+y,1/2-z ; (f) : 1-x,-1/2+y,1/2-z

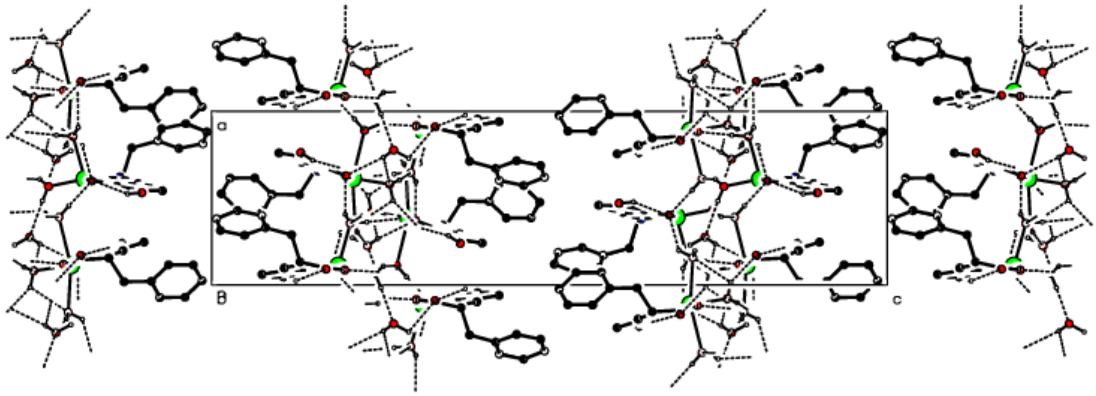


Fig 3. 2D supramolecular network of the compound along the a and b axes (viewed along the b axis). Selected H atoms omitted for clarity

3.2 Thermogravimetric analysis

With a view to determine the relative ease of loss of the coordinated and non-coordinated water molecules, thermogravimetric analysis was carried out. The TGA and DTA curves of the product are given in Figure 4. It was noticed that loss of water began immediately on the initiation of heating and occurred in two stages. Thus, between 29 ^{o}C and 95 ^{o}C, a weight loss of 9.0 % had occurred (4.5 % calculated for loss of 2 H_2O). Subsequently, between 95 ^{o}C and 235 ^{o}C, a further weight loss of 4.5 % had occurred. Thus it seems reasonable to assume that initially, the water of crystallisation and three coordinated water molecule had been lost affording two square planar $LM(H_2O)$ fragments, from which the final water molecules were considerably more difficult to remove.

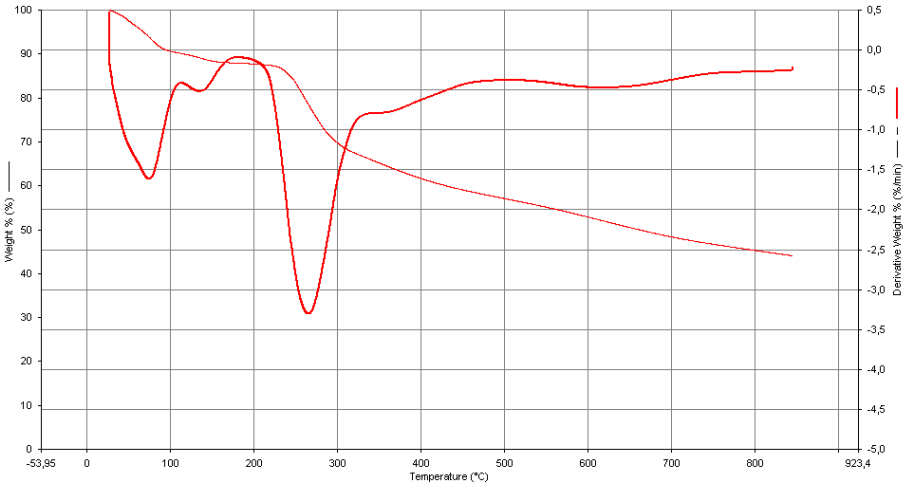


Fig 4. TGA-DTA curves of the title compound, $L_2Cu_2(H_2O)_5.H_2O$.

4. Acknowledgements

This work has been completed at Dokuz Eylül University and is the subject of the forthcoming Ph.D. Thesis of Duygu Barut.The authors acknowledge Dokuz Eylül University for the use of the Agilent Xcalibur Eos diffractometer (purchased under University Research Grant No: 2010.KB.FEN.13).

5. Supplementary material

Crystallographic data as .cif files for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center with CCDC 985068. Copies of the data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK). Email: deposit@ccdc.cam.ac.uk.

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