

Scientific paper

Synthesis, X-ray Structural and Thermal Analysis of a Novel Copper Compound Containing Dissymmetric Independent 5- and 6-coordinate $\text{CuL}(\text{H}_2\text{O})_n$ ($n = 2, 3$) Units and Hydrogen bond Bridges

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Received: 12-06-2014

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 $[\text{CuL}(\text{H}_2\text{O})_2] \cdot [\text{CuL}(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ crystallizes in the orthorhombic crystal system in space group $P2_12_12_1$ with $Z = 4$. The two independent $\text{CuL}(\text{H}_2\text{O})_n$ complexes are present in the same unit cell, along with an uncoordinated water molecule. The five-coordinated copper(II) centre occupies a distorted square-pyramidal geometry whereas the six-coordinated 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} oligo-

nuclear,^{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 in the investigation of the copper(II) complexation behaviour towards a tridentate Schiff base ligand (*L*) derived from phenylalanine and 2,4-dihydroxybenzaldehyde resulted in a structure that contains two independent Cu(II)L(H₂O)_n 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 is 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 simply by a differing degree of solvent association. 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

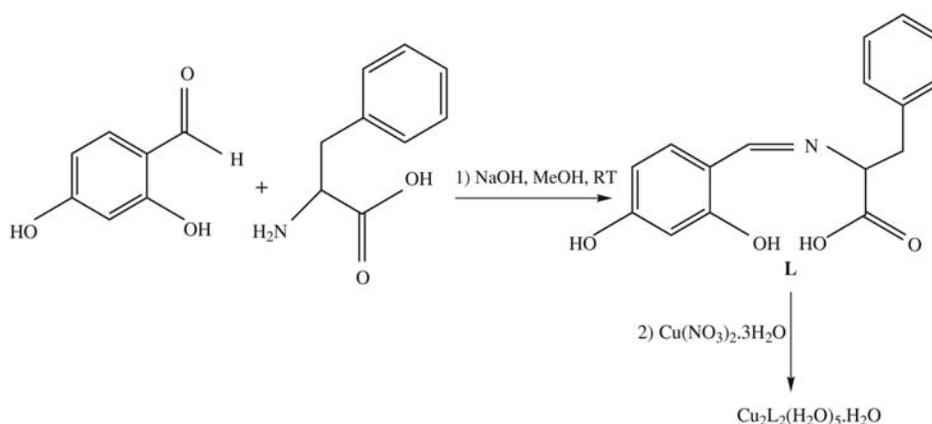
2. 1. Synthesis of the Title Complex

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, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (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 [$R_f = 0.65$, (EtOAc : MeOH = 3 : 2)], the solvent was removed. Bright green cry-

stals were obtained after crystallization from MeOH by addition of a small amount of water. Yield: 0.23 g, 58 %. Anal. Calc. for (%) $\text{C}_{32}\text{H}_{38}\text{Cu}_2\text{N}_2\text{O}_{14}$ ($\text{Cu}_2\text{L}_2(\text{H}_2\text{O})_6$, 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): 3368 (br, O-H), 2912 (w, C-H), 1607 (m, C=N), 1548 (s, CO_2 asym), 1496 (s, CO_2 asym), 1451 (m, CO_2 sym), 1354 (m, CO_2 sym), 1289 (m, O-H), 1227 (w), 1123 (w), 991 (w), 707 (w) cm^{-1} (Scheme 1).

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 with Mo- $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation and a grap-



Scheme 1. The synthetic method for the preparation of $\text{Cu}_2\text{L}_2(\text{H}_2\text{O})_5 \cdot \text{H}_2\text{O}$.

Table 1. Crystal data and structural refinement parameters

Crystal Data	
Empirical Formula	$[\text{CuC}_{16}\text{H}_{19}\text{NO}_7][\text{CuC}_{16}\text{H}_{17}\text{NO}_6] \cdot \text{H}_2\text{O}$
Formula Weight [g/mol]	801.72
Cell setting / Space group	Orthorhombic / $P2_12_12_1$
Unit cell dimensions [\AA]	$a = 9.0840(6)$ $b = 10.9080(5)$ $c = 35.416(2)$
Unit cell volume	$3509.3(3) \text{ \AA}^3$
Temperature [K]	293
Absorption coefficient [mm^{-1}]	1.282
Z / Density [g/cm^3]	4 / 1.52
F (000)	1656
Crystal size [mm^3]	$0.6 \times 0.2 \times 0.1$
θ range [$^\circ$]	2.96–26.37
h range	–11 → 6
k range	–13 → 7
l range	–43 → 43
Reflections collected / unique	9036 / 6069
Goodness-of-fit on F^2	1.184
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.066$, $wR_2 = 0.112$
R indices all data	$R_1 = 0.084$, $wR_2 = 0.123$
Large diff. peak and hole	0.44 / –0.58

hite monochromator. Data were absorption-corrected within the CrysAlis program.²⁶ The structure was solved by SHELXS-97 and refined by means of SHELXL-97 program²⁷ incorporated in the OLEX2 program package.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.

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

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 oxygen 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, leading to distorted octahedral geometry.^{32,33} However, 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 within the expected range for apically bonded water molecules,^{16,17} and 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 indicates that most bond lengths are very similar (Table 2) and are entirely consistent with those observed in the literature.^{34–37} 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 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).

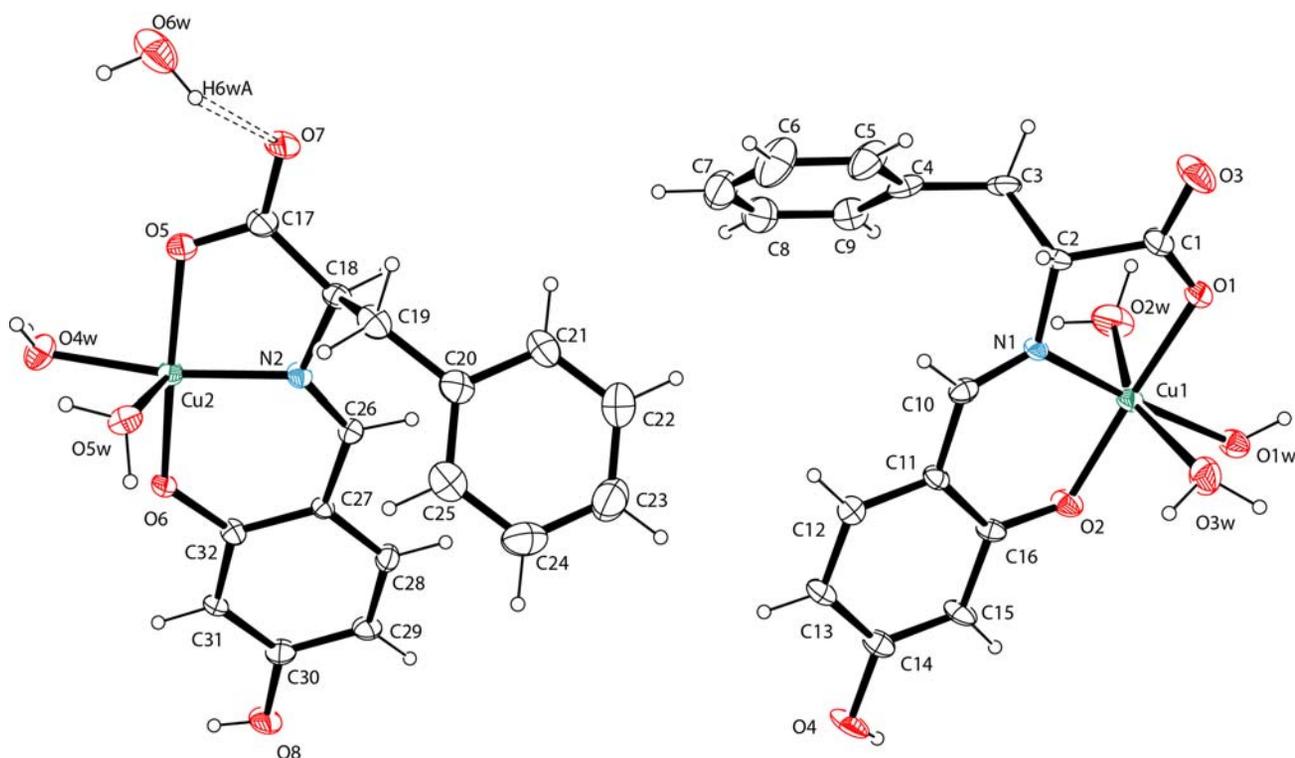


Fig 1. The molecular structure of the title compound in the asymmetric unit, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed line indicates the inter-molecular hydrogen bond.

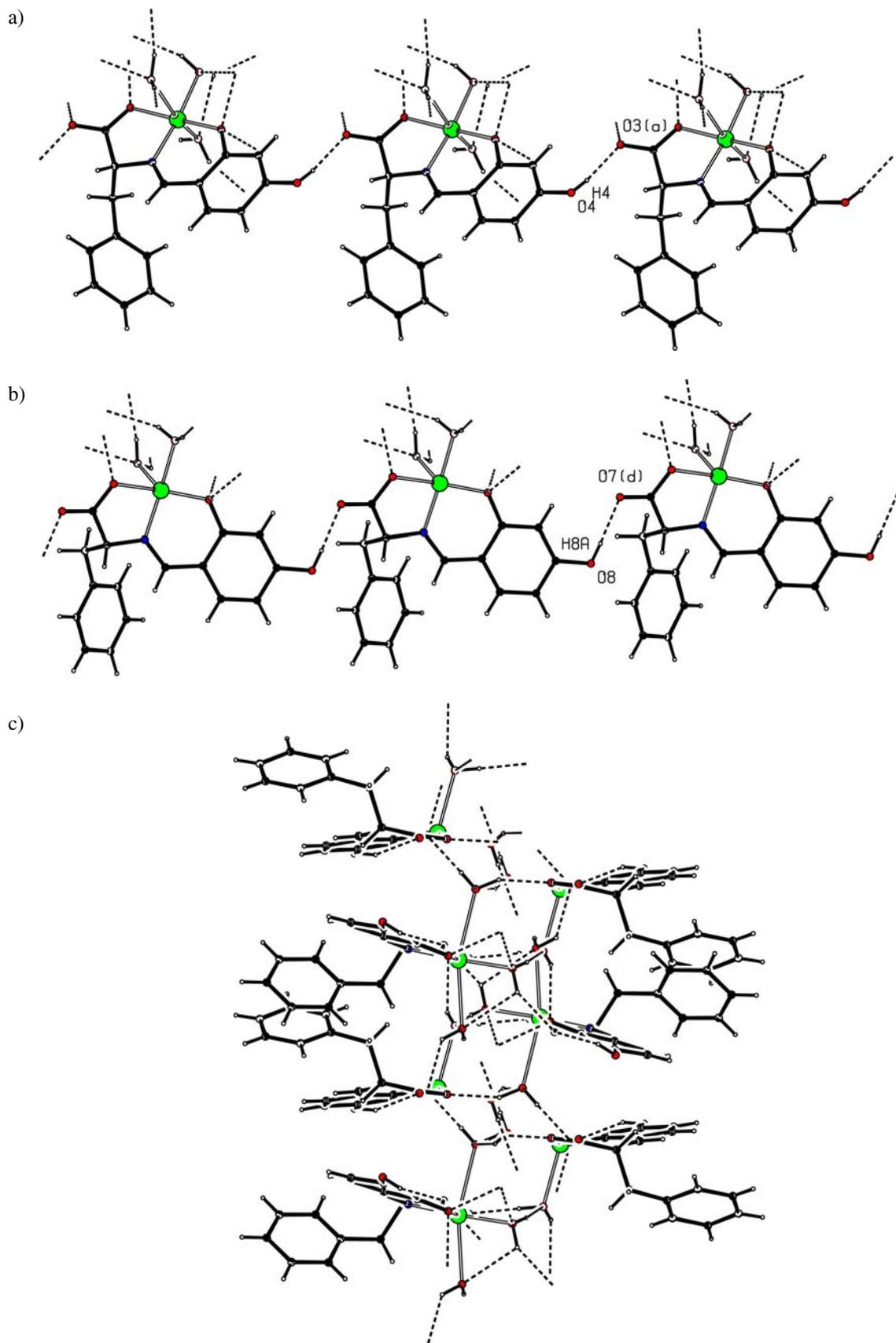


Fig 2. Intermolecular O–H...O hydrogen bonding: (a) and (b) link the molecules into infinite chains along the *b* axis and (c) link the two adjacent copper molecules into infinite chains along the *a* axis (see Table 3 for further details).

Table 2. Selected interatomic distances (Å) and bond angles (°)

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)		

In the crystal structure, both copper complexes form a one-dimensional infinite chain *via* O4–H4···O3 and O8–H8A···O7 hydrogen bonds along the *b* axis (Table 3, 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.^{38,39} There are intermolecular O–H···O hydrogen bonds observed between adjacent copper molecules (Table 3, entries 2, 5, 6, 8, 10) forming supramolecular ribbons along the *a* axis (Fig. 2c). Furthermore, the uncoordinated water molecule is connected to copper molecules *via* O–H···O hydrogen bonds to form a two-dimensional su-

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

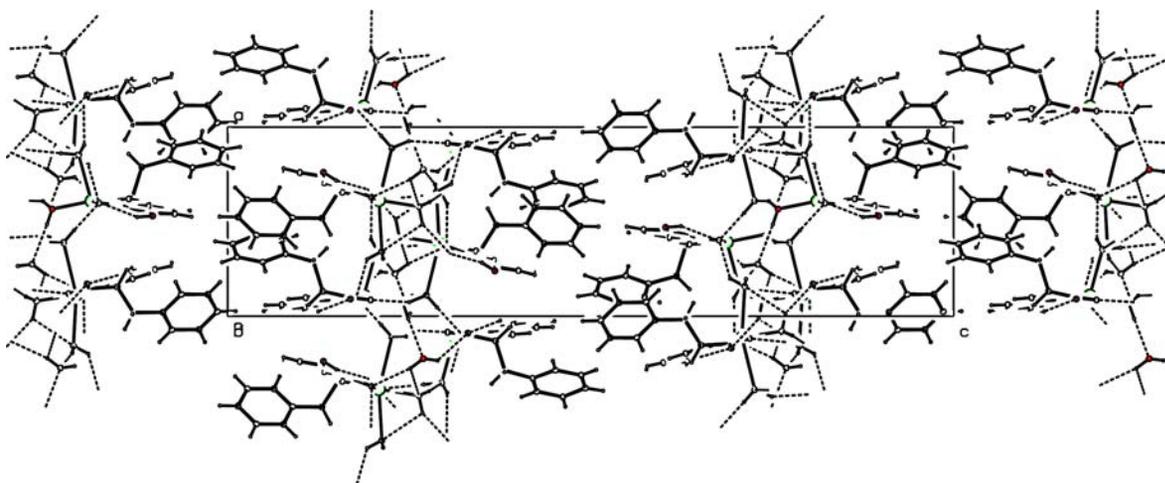
Bond	D–H	H···A	D···A	D–H···A
O4–H4···O3 ^a	0.82	1.85	2.654 (8)	165
O1w–H1wA···O5w ^b	0.89	2.12	2.971 (6)	161
O1w–H1wB···O3 ^b	0.89	2.18	2.968 (7)	147
O2w–H2wA···O6w	0.91	1.92	2.812 (8)	166
O3w–H3wB···O6 ^c	0.90	1.97	2.869 (7)	175
O3w–H3wA···O5 ^b	0.90	1.96	2.759 (6)	147
O8–H8A···O7 ^d	0.82	1.92	2.694 (7)	157
O4w–H4wA···O3w ^f	0.79	2.26	2.942 (8)	145
O4w–H4wB···O6w ^c	0.77	2.07	2.830 (9)	170
O5w–H5wB···O1 ^f	0.87	1.85	2.717 (6)	173
O6w–H6wB···O2 ^f	0.85	2.16	2.990 (8)	167

Symmetry codes: (a) *x*, 1 + *y*, *z*; (b) 1 – *x*, ½ + *y*, ½ – *z*; (c) 1 + *x*, 1 + *y*, *z*; (d) *x*, –1 + *y*, *z*; (e) –*x*, –½ + *y*, ½ – *z*; (f) 1 – *x*, –½ + *y*, ½ – *z*.

pramolecular network which lies parallel to the *ab* plane. This plane and the packing of the complexes can be seen in Fig. 3.

3. 2. Thermogravimetric Analysis

With the aim 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 °C and 95 °C, a weight loss of 9.0% had occurred (9.0% calculated for loss of 4 H₂O). Subsequently, between 95 °C and 235 °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(H₂O) fragments, from which the final water molecules were considerably more difficult to remove.

**Fig 3.** 2D supramolecular network of the compound along the *ab* plane (viewed along the *b* axis). Selected H atoms have been omitted for clarity

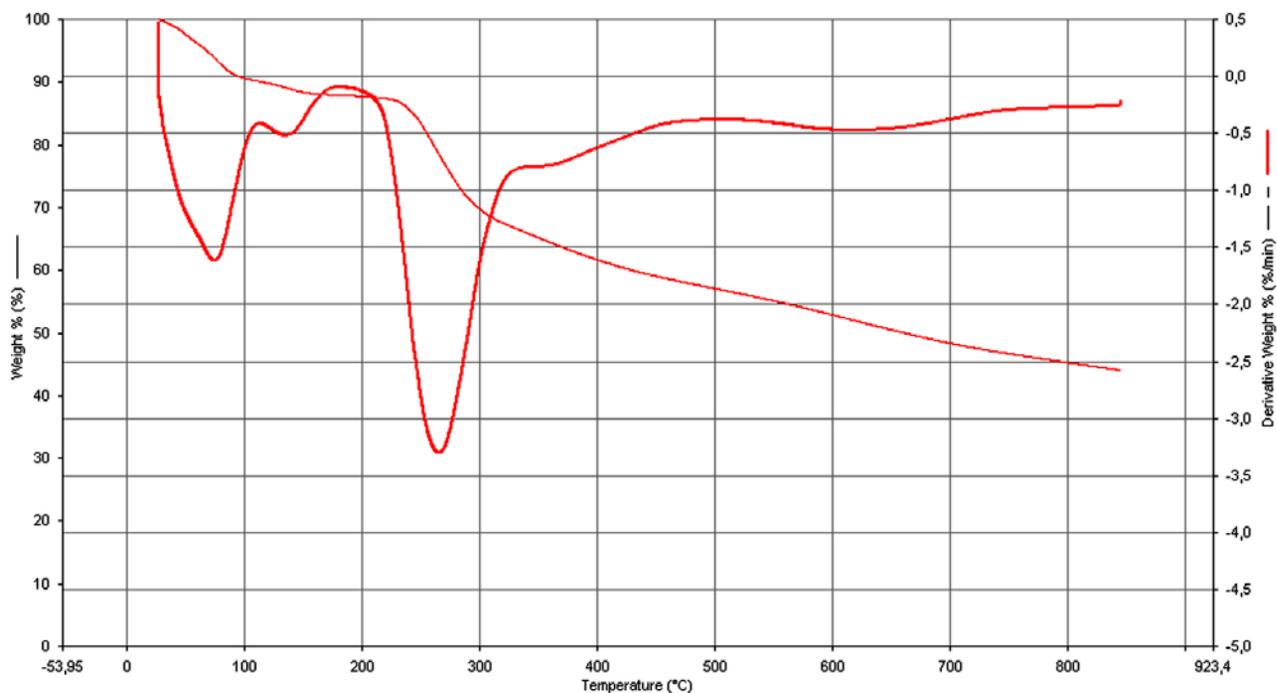


Fig 4. TGA-DTA curves of the title compound $\text{Cu}_2\text{L}_2(\text{H}_2\text{O})_5 \cdot \text{H}_2\text{O}$.

4. Conclusions

X-ray structural analysis of a novel compound containing pentacoordinated and hexacoordinated copper complexes shows that the axially coordinated water ligands of the octahedral complex [bond lengths of 2.473(6) Å and 2.593(6) Å] are bound in a significantly weaker fashion than the apically coordinated water molecule [bond length of 2.320(4) Å] of the pentacoordinate complex. Overall, these results experimentally confirm that in this case, and possibly for many other Cu(II) complexes, there is only a very small energy difference between octahedral and square pyramidal geometries, which in turn, demonstrates how pentacoordinated copper(II) complexes can readily associate substrate moieties.

5. 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).

6. Supplementary Material

Crystallographic data as cif file for the structure reported in this paper have been deposited at the Cambrid-

ge 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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Povzetek

Izvedena je bila sinteza ter termogravimetrična in rentgenska strukturna analiza nenavadne bakrove spojine pripravljene z vezavo kiralne trovezne Schiffove baze kot liganda na bakrove ione. Spojina $[\text{CuL}(\text{H}_2\text{O})_2] \cdot [\text{CuL}(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ kristalizira v ortorombskem kristalnem sistemu v prostorski skupini $P2_12_12_1$ z $Z = 4$. Dva kristalografsko neodvisna $\text{CuL}(\text{H}_2\text{O})_n$ kompleksa sta prisotna v asimetrični enoti skupaj nekoordinirano molekulo vode. Pentakoordiniran bakrov(II) center ima popačeno kvadratno-piramidalno geometrijo, medtem ko ima heksakoordiniran bakrov(II) center popačeno oktaedrično geometrijo. Oba bakrova kompleksa in nekoordinirana molekula vode so med seboj povezani z intermolekularnimi vodikovimi vezmi v dvo-dimenzionalno supramolekularno mrežo, ki leži vzporedno z *ab* ravnino.