New One-Pot Synthetic Route and Spectroscopic Characterization of Hydroxo-Bridged Stepped-Cubane Copper(II) Complexes

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ABSTRACT

A new convenient and efficient route for the synthesis of two very important hydroxo-bridged stepped-cubane copper complexes viz: $[Cu_4(bpy)_4Cl_2(OH)_4]Cl_2.6H_2O$ (**1**) and $[Cu_4(phen)_4Cl_2(OH)_4]Cl_2.6H_2O$ (**2**) have been obtained. This synthetic route from the mononuclear $CubpyCl_2$ complex is easier, more reproducible and afforded the complex in a much higher yield than the other two previously reported procedures which were equally serendipitously discovered. The purity and formation of the complexes were confirmed with elemental (C,H,N) analysis and the details of the UV-Vis, Fourier transform infrared, electrospray ionization mass spectra of both complexes and the single crystal X-ray crystallography of **1** are presented and discussed. X-ray crystallography confirms the absolute structure of the complexes. The complexes were formed via the connection of four copper atoms to four hydroxide bridging ligands and four bipyridyl ligands with two chloride ligands. There are two coordinate environments around two pairs of copper atoms (CuN_2ClO_2 and CuN_2O_3) and each copper atom is pentacoordinate with square pyramidal geometry.

Keywords: Copper; Tetranuclear; Cubane; Synthesis; Complexes; Spectroscopy.

1. INTRODUCTION

Preponderance of metals in nature propels their uses as crucial components of enzymes and as catalyst for most biological reactions. In particular, transition metals, their alloys and other metallic compounds have extensive uses in our daily lives, in medical sector and as catalysts in a variety of industrial processes because of their unique and tunable properties. Metals and their compounds have also been widely applied as materials for memory and data storage; they play key roles in electrochemical sensor devices in addition to their uses as drugs and diagnostic tools [1],[2].

Transition metals such as copper and their compounds feature significantly in biological systems by directing the geometry of enzymatic active sites, acting as enzyme activators, and facilitating reactions of enzymes by shutting electrons out or by helping to bind to substrate. For instance, copper is an essential trace element that constitutes important cellular components and plays crucial roles in important biological, technological and industrial processes.

The distinctive and diverse properties of metal complexes have been widely employed in the application of metal-containing medicinal agents, diagnostic tools which can be used to quantify detect, or affect biological processes at microscopic level [3].

Currently, scientists are designing a wide range of metal complexes to advance new therapeutics with custom-made designs and features that model the desirable properties of biomolecules. Polynuclear Cu(II) complexes are a class of complexes with rich versatile structural varieties and magnetic properties which elicit their interesting applications in bio-inorganic chemistry, catalysis and magnetism [4-7]. Examples of such metal complexes which have considerable importance are cubane complexes with Cu_4O_4 chromophore which possess rich magnetic and

structural properties that have enabled their applications as single molecule magnets [8],[9] in biological inorganic chemistry [4],[7],[10] and in catalysis [9],[10],[13]. Such metal complexes have been widely applied as efficient water oxidation electrocatalysts in aqueous alkaline conditions because of their similarities to natural oxygen-evolving complex (OEC) in photosystem II [11],[12]. Some of these complexes have also been tested as catalysts [9],[10], and as DNA binding and nuclease agents [5],[7],[10].

In this present study, based on the crucial roles of copper complexes and the afore-mentioned applications of tetranuclear copper cubane complexes, we report new one-pot, efficient, reproducible synthetic method for hydroxo-bridged stepped cubane complexes *viz:* $[Cu_4(bpy)_4Cl_2(OH)_4]Cl_2.6H_2O$ (**1**) and $[Cu_4(phen)_4Cl_2(OH)_4]$ $Cl_2.6H_2O$ (**2**). The ESI-MS, UV-Vis and FTIR spectra of hydroxo-bridged stepped-cubane copper complexes corroborates the synthesis of the complexes in good yield.

2. MATERIALS AND METHODS

2.1. Materials

Analytical grade reagents and solvents were purchased from VWR International and used without further purification. Elemental (C, H and N) analyses were carried out using standard methods with Elementar Analysen Systeme Vario® MICRO VI 6.2 GmbH. UV–Vis spectra were measured using a JASCO V-730 UV-Vis spectrophotometer. FTIR spectra were recorded in a range of 4,000–400 cm^{-1} on Shimadzu FTIR-8400S instrument. Melting points were taken on a Jenway analytical instrument and were uncorrected. The electrospray mass spectra were recorded on a THERMO Finningan LCQ Advantage max ion trap mass spectrometer. The single-crystal X-ray diffraction data for 1 were collected at room temperature using Mo-Kα radiation. All measurements were taken at room temperature.

2.2. Synthesis

2.2.1. Synthesis of precursor complexes

CubpyCl₂

CubpyCl₂was prepared by the following procedure. 0.0937 g (0.6 mmol) of 2, 2'-bipyridine was added to a solution of 0.100g (0.6 mmol) of $CuCl_2.2H_2O$ in 30 ml acetonitrile and the solution stirred for 1 hour. The precipitated light green powder was filtered and dried in vacuum desiccator. FT-IR (KBr, v/cm^{-1}): 3107, 3066, 3053, 3034, 1600, 1568, 1496, 1471, 1444, 1417, 1319, 1284, 1246, 1219, 1159, 1116, 1058, 1026, 974, 906, 804, 777, 729, 659, 634, 474, 441, 418. UV-Vis (H_2O, nm): 300, 310, 369, 743. UV-Vis (CH_3CN, nm): 242, 269, 298, 727, 746.

CuphenCl₂

CuphenCl₂was prepared by the following procedure. 0.1190 g (0.6 mmol) of 1, 10-phenthroline was added to a solution of 0.100g (0.6 mmol) of $CuCl_2.2H_2O$ in 30 ml acetonitrile and the solution stirred for 1 hour. The precipitated light green powder was filtered and dried in vacuum desiccator. FT-IR (KBr, v/cm^{-1}): 3078, 33057, 3043, 3012, 1626, 1606, 1583, 1514, 1494, 1423, 1348, 1222, 1199, 1145, 1107, 1047, 987, 902, 856, 779, 736, 721, 644, 542, 430.

2.2.2. Synthesis of complexes

$[Cu_4(bipy)_4Cl_2(OH)_4]Cl_2.6H_2O$ (1)

A mixture of 0.231 g (0.5 mmol) of lincomycin hydrochloride monohydrate, 0.144 g (0.5 mmol) of CubpyCl$_2$ and 0.2 ml of triethyl amine in 5 ml of methanol was allowed to stand for one week. The blue precipitated crystals were filtered and purified with about 10 ml methanol. Calculated: C, 40.14; H, 4.04; N, 9.36. Found: C, 40.22; H, 4.57; N, 8.96. UV-Vis (H$_2$O, nm): 235, 300, 311, 341, 370, 401, 618. FT-IR (KBr, ν/cm^{-1}): 3437, 3362, 3111, 3076, 3026, 1627, 1602, 1475, 1444, 1323, 1253, 1220, 1163, 1105, 1028, 997, 910, 810, 771, 731 690, 659, 628, 567, 545, 489, 472, 437, 414. Melting point: 165 ^{o}C (dec).

$[Cu_4(phen)_4Cl_2(OH)_4]Cl_2.6H_2O$ (2)

A mixture of 0.231 g (0.5 mmol) of lincomycin hydrochloride monohydrate, 0.157 g (0.5 mmol) of CuphenCl$_2$ and 0.2 ml of triethyl amine in 5 ml of methanol was allowed to stand for one week. The blue precipitated crystals were filtered and purified with about 10 ml methanol. Calculated: C, 45.22; H, 3.64; N, 8.79. Found: C, 45.07; H, 3.89; N, 8.77. UV-Vis (H$_2$O, nm): 204, 272, 294, 389, 639. FT-IR (KBr, ν/cm^{-1}): 3412, 3335, 3236, 3055, 2939, 2875, 2675, 2492, 1630, 1585, 1518, 1429, 1311, 1145, 1103, 1049, 991, 852, 723, 607, 430. Melting point: 178 ^{o}C (dec)

3. RESULT AND DISCUSSION

3.1. Spectroscopic Characterization

In an attempt to synthesize ternary Cu^{II} complexes of lincomycin with bipyridine and phenanthroline, stepped cubane tetranuclear hyroxo bridged Cu^{II} complexes of the polypyridyl ligands were obtained. The UV-Vis, FT-IR, ESI-Mass spectra of both complexes **1** and **2** and single crystal date of **1** have been obtained. Table 1 summarizes the yield, physic-chemical and UV-Visible spectroscopic characterization of the complexes. The complexes exhibit π-π^*, metal-ligand charge transfer and d-d transitions. The d-d transitions for complexes **1** and **2** were at 618 and 639 nm respectively and are characteristic of a square pyramidal geometry around copper. The first example of an hydroxo-bridged tetranuclear cubane-like copper(II) complex with a Cu$_4$(OH)$_4$ core was [Cu(2,2'-bipy)(OH)]$_4$(PF$_6$)$_4$ [14].

Table 1. UV-Vis and physico-chemical data of complexes **1** and **2**

Compound	λ_{max} (nm)	Transition	Yield (%)	Colour	Melting Point (^{o}C)
1	235	π-π^*	85	blue	165
	300,311, 341, 370, 401	MLCT			
	618	d-d			
2	204, 272, 294	π-π^*	82	blue	178
	389	MLCT			
	639	d-d			

In the FT-IR spectra of **1** strong absorption bands arising from O-H stretching vibration of both the hydroxo bridging ligands and aqua outside the coordination sphere appear at 3437 and 3362 cm^{-1}. Sharp bands at 1602, 1501, 1475 and 1440 cm^{-1} arose from the alkene and imine vibrational stretching of bipyridine. The vibration (weak) at about 950 cm^{-1} is due to O-H bend. The band at 489 cm^{-1} is assigned to copper-oxygen vibration as it falls in the same range (480-515 cm^{-1}) with what is previously reported for hydroxyl-bridge Cu^{II} complexes. For **2**, the band at 771 cm^{-1} is from imine C-N stretching of 1,10-phenanthroline while the stretching frequencies of both the hydroxo bridging ligands and aqua outside the coordination sphere appeared at 3412 and 3335 cm^{-1}. Alkene and imine stretching frequencies of 1,10-phenanthroline are found at 1630 cm^{-1}and at 1585 and 1518 cm^{-1} respectively.

The ESI-MS of complexes **1** and **2** provide additional evidence for the formation of the complexes with the observed daughter ion peaks from the complexes. The peak at 512.0 (calculated: 509.2) in Complex **1** corresponds to $[Cu_4bpy_4Cl_2(OH)_4]^{2+}$. Complex **2** showed a peak corresponding to $[Cu_2phen_2Cl(OH)_2]^{2+}$ at 557 (calculated: 556.592). Peaks at 278.0, 310.0 and 375.0 (calculated: 279, 313 and 376.6) correspond to CuphenCl, [CuphenCl(OH)$_2$] and [CuphenCl(OH)$_2$ +Cu] respectively.
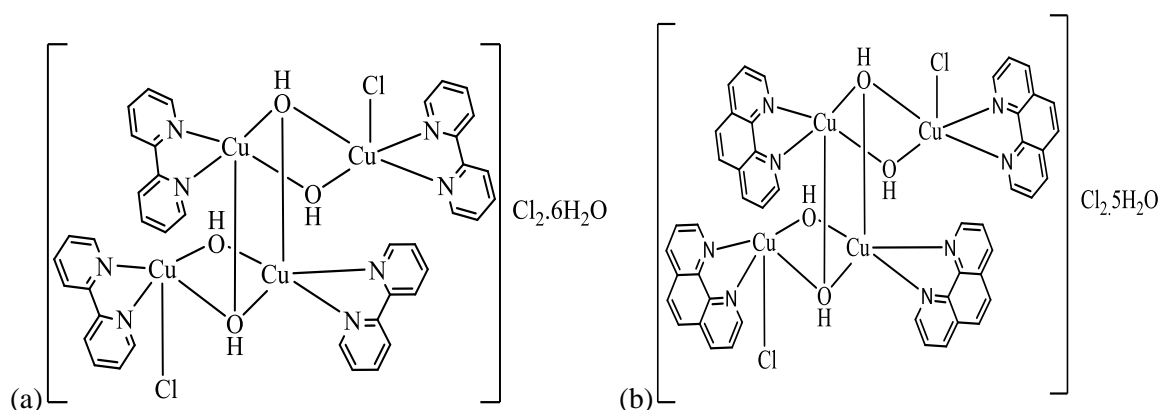
Figure 1. Structures of (a) [Cu$_4$(bpy)$_4$Cl$_2$(OH)$_4$]Cl$_2$.6H$_2$O (1), and (b) [Cu$_4$(phen)$_4$Cl$_2$(OH)$_4$]Cl$_2$.6H$_2$O (2)

3.2. Single Crystal Analysis

The crystal structure of complex **1** has been solved and described previously [12],[13]. The complexes are typical examples of tetranuclear copper(II) with Cu$_4$(OH)$_4$ core. The asymmetric unit possesses both μ_2-OH and μ_3-OH and the structure of the compounds have chair-like stepped cubane structure. Two crystallographically independent pentacoordinate copper atoms are found in the two complexes. The two copper atoms possess different environments: CuN$_2$O$_3$ and CuN$_2$O$_2$Cl though the two coordination arrangements are square pyramids.

Even though the crystal structure of complex **1** has been previously reported, we have serendipitously obtained a new route for the synthesis of this very important stepped-cubane complex. This synthetic route from the mononuclear CubpyCl$_2$ is easier, more reproducible and afforded the complex in a much higher yield than the other two previously reported procedures [15,[16] of which the latter was also serendipitously discovered.

Crystallographic data showing the π-π stacking interaction and hydrogen bonding in the complex **1** have also been collected and are presented in **Figure 2**. The structure contains centrosymmetric [Cu$_4$(bpy)$_4$Cl$_2$(OH)$_4$]$^{2+}$ cations. Each Cu(II) ion has five-coordinate, square pyramidal geometry and is coordinated to one bidentate bpy and two

bridging hydroxo donors in the basal plane. The coordination sphere of Cu1 is completed by a chloride ion, while Cu2 is coordinated to a μ_3-OH, linking the two halves of the dimer together (under symmetry operation -x+2,-y+2,-z+2). There is also a π-π interaction between the bpy ligands (mean interplanar distance 3.38 Å). The bond lengths and angles are unexceptional; as might be expected the Cu-OH bonds are longer to the μ_3-OH group than to the μ_2-OH bridge and the apical Cu-OH bond is considerably longer than the basal plane values. The Cu1 – Cu2 distance in the $Cu_2(OH)_2$ unit is 2.897(4)Å. The hydroxo and chloro ligands, together with the solvate water molecules are involved in hydrogen bonding, generating 2D sheets in which the cations are linked by H-bonded rings. The sheets are linked via intermolecular π-stacking.
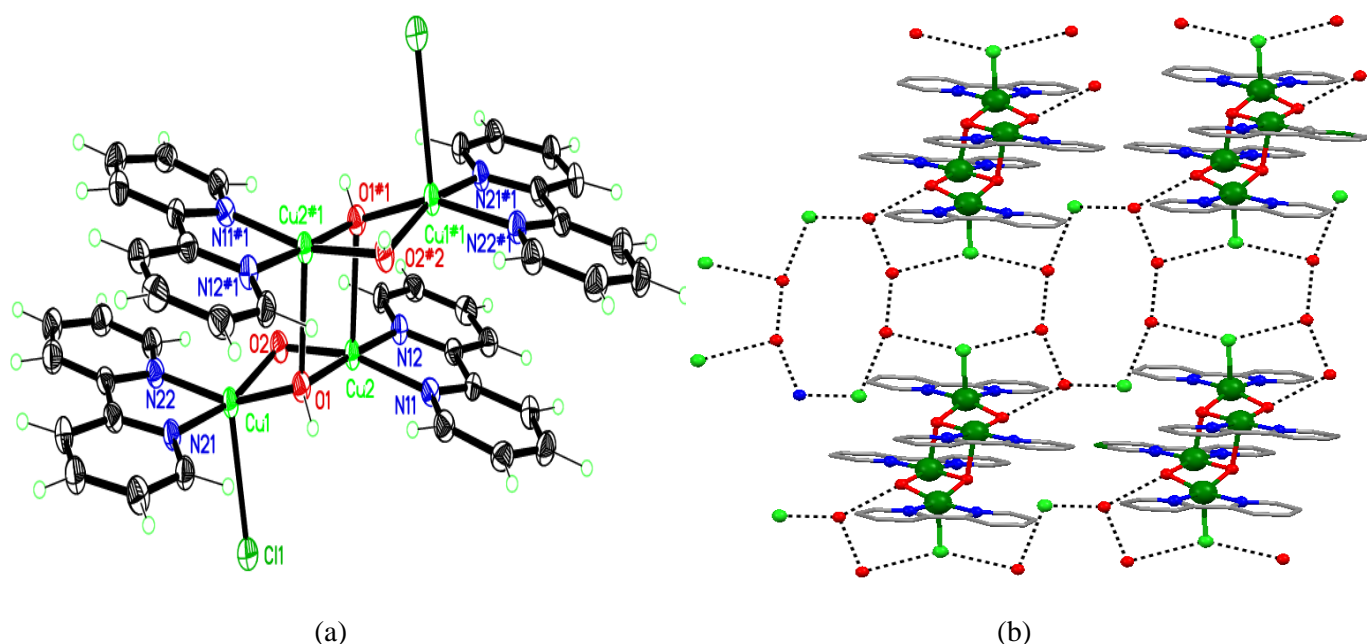

(a)   (b)

Figure 2. Crystal structure of $Cu_4(bipy)_4Cl_2(OH)_4]\cdot Cl_2\cdot 6H_2O$ of (1): (a) at 50% ellipsoids; (b) H-bond sheet

(c)   (d)
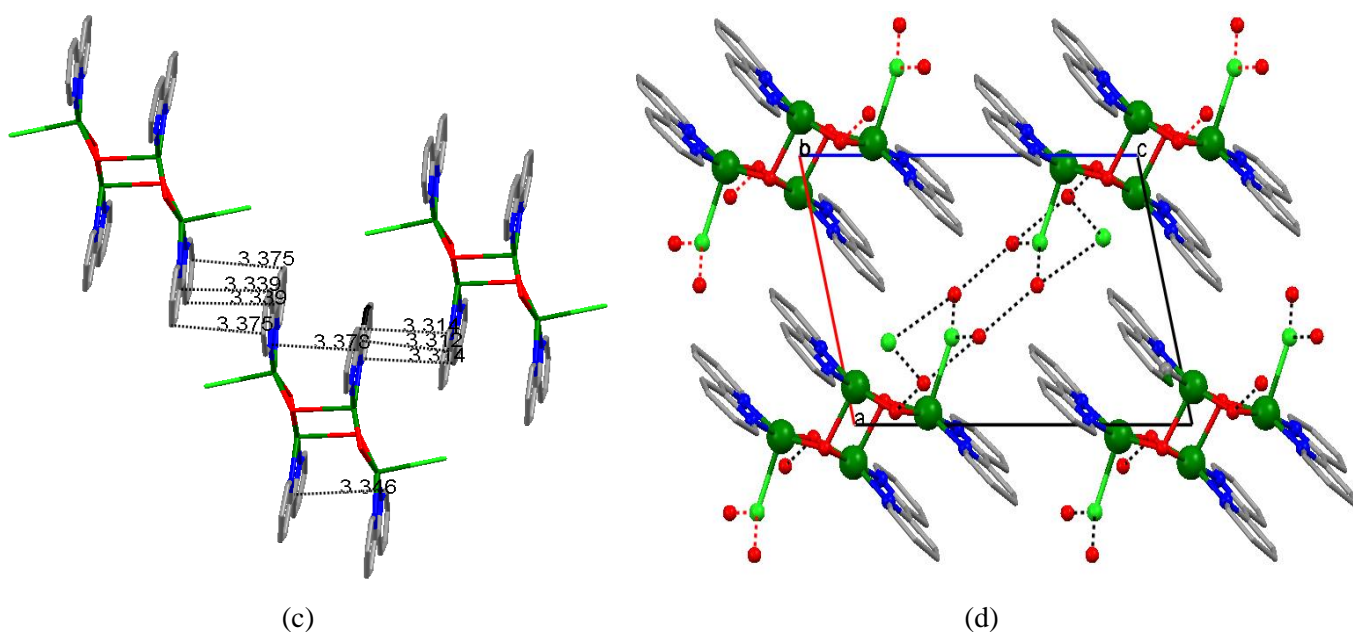
Figure 2. contd.: Crystal structure of $Cu_4(bipy)_4Cl_2(OH)_4]Cl_2\cdot 6H_2O$ (c) π-π stacking; (d) Packing plot viewed down b axis

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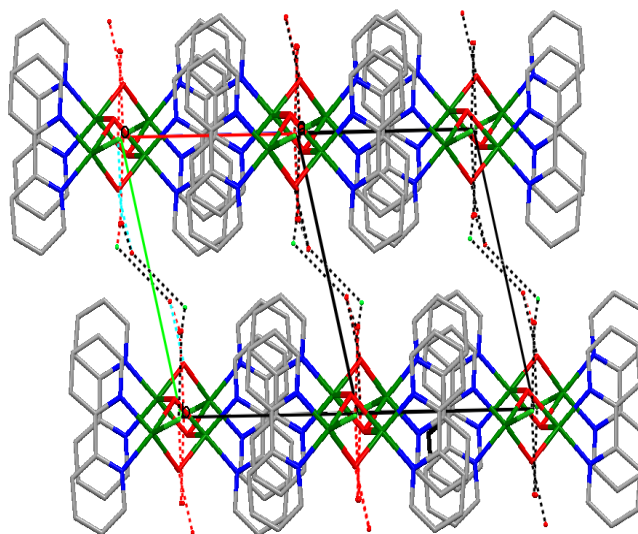
(e)

Figure 2. contd.: Crystal structure of $Cu_4(bipy)_4Cl_2(OH)_4]Cl_2 \cdot 6H_2O$ (e) Packing plot showing π-stacking

Table 2. Selected bond lengths [Å] and angles [°] for complex **1**

	Bond lengths [Å]
Cu(1)-O(2)	1.906(4)
Cu(1)-O(1)	1.954(4)
Cu(1)-N(21)	1.981(4)
Cu(1)-N(22)	2.008(4)
Cu(1)-Cl(1)	2.525(4)
Cu(1)-Cu(2)	2.897(4)
Cu(2)-O(2)	1.908(4)
Cu(2)-O(1)	1.938(4)
Cu(2)-N(12)	1.970(4)
Cu(2)-N(11)	1.986(4)
Cu(2)-O(1)#1	2.281(4)
	Bond angles [°]
O(2)-Cu(1)-O(1)	80.83(19)
O(2)-Cu(1)-N(21)	165.69(14)
O(1)-Cu(1)-N(21)	96.77(19)
O(2)-Cu(1)-N(22)	96.34(19)
O(1)-Cu(1)-N(22)	157.33(15)
N(21)-Cu(1)-N(22)	80.4(2)

O(2)-Cu(1)-Cl(1)	99.60(13)
O(1)-Cu(1)-Cl(1)	99.16(13)
N(21)-Cu(1)-Cl(1)	94.71(15)
N(22)-Cu(1)-Cl(1)	103.48(16)
O(2)-Cu(2)-O(1)	81.20(18)
O(2)-Cu(2)-N(12)	97.99(19)
O(1)-Cu(2)-N(12)	177.24(14)
O(2)-Cu(2)-N(11)	166.11(14)
O(1)-Cu(2)-N(11)	99.09(18)
N(12)-Cu(2)-N(11)	81.1(2)
O(2)-Cu(2)-O(1)#1	99.68(17)
O(1)-Cu(2)-O(1)#1	85.53(16)
N(12)-Cu(2)-O(1)#1	97.21(17)
N(11)-Cu(2)-O(1)#1	94.18(18)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+2,-z+2

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2x 10^3) for **1**. U(eq) is

defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Cu(1)	10440(1)	10540(1)	7755(1)	19(1)
Cu(2)	11399(1)	10664(1)	9741(1)	18(1)
N(11)	12832(4)	9368(4)	10542(3)	19(1)
C(10)	13171(5)	8004(4)	10555(4)	23(1)
C(11)	14239(5)	7187(5)	11081(4)	25(1)
C(12)	14965(6)	7795(5)	11644(4)	27(1)
C(13)	14618(6)	9196(5)	11653(4)	25(1)
C(14)	13555(5)	9955(4)	11084(3)	19(1)
C(15)	13101(5)	11450(4)	11025(3)	20(1)
C(16)	13712(6)	12259(5)	11527(4)	25(1)
C(17)	13179(6)	13648(5)	11423(4)	26(1)
C(18)	12064(6)	14210(5)	10863(4)	24(1)
C(19)	11511(5)	13356(4)	10381(4)	23(1)

N(12)	12024(4)	12003(4)	10455(3)	19(1)
N(21)	9837(4)	9228(4)	6983(3)	19(1)
C(20)	10307(5)	7877(4)	7055(4)	22(1)
C(21)	9823(6)	7034(5)	6502(4)	25(1)
C(22)	8819(6)	7623(5)	5850(4)	26(1)
C(23)	8326(6)	9028(5)	5759(4)	24(1)
C(24)	8865(5)	9800(4)	6334(3)	21(1)
C(25)	8446(5)	11293(4)	6279(3)	20(1)
C(26)	7418(6)	12071(5)	5698(4)	27(1)
C(27)	7101(6)	13476(5)	5707(4)	28(1)
C(28)	7815(6)	14049(5)	6291(4)	27(1)
C(29)	8828(6)	13218(5)	6866(4)	24(1)
N(22)	9131(4)	11863(4)	6866(3)	20(1)
O(1)	10868(4)	9349(3)	8978(2)	19(1)
O(2)	10491(4)	11874(3)	8712(2)	21(1)
Cl(1)	13245(1)	10068(1)	6588(1)	28(1)
Cl(2)	13053(1)	16094(1)	8498(1)	27(1)
O(3)	11533(4)	14112(3)	7700(3)	28(1)
O(4)	15168(5)	13076(4)	3749(3)	42(1)
O(5)	13274(5)	13048(4)	5774(3)	43(1)

Table 4. Hydrogen bonds for complex **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...Cl(2)#2	0.809(19)	2.55(2)	3.341(6)	166(5)
O(2)-H(2)...O(3)	0.81(2)	2.04(3)	2.820(6)	162(5)
O(3)-H(3A)...O(5)	0.836(19)	1.86(2)	2.674(6)	164(5)
O(3)-H(3B)...Cl(2)	0.831(19)	2.28(2)	3.094(5)	168(5)
O(4)-H(4A)...Cl(2)#3	0.832(19)	2.35(4)	3.108(6)	152(6)
O(4)-H(4B)...Cl(1)#4	0.829(19)	2.29(2)	3.117(7)	174(5)
O(5)-H(5A)...O(4)	0.817(19)	1.97(3)	2.723(7)	153(5)
O(5)-H(5B)...Cl(1)	0.841(19)	2.32(2)	3.142(7)	167(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,-z+2   #2 x,y-1,z   #3 -x+3,-y+3,-z+1   #4 -x+3,-y+2,-z+1

▓ 4. CONCLUSION

Two very important hydroxo-bridged stepped-cubane copper(II) complexes *viz:* $[Cu_4(bpy)_4Cl_2(OH)_4]Cl_2.6H_2O$ (**1**) and $[Cu_4(phen)_4Cl_2(OH)_4]Cl_2.6H_2O$ (**2**) have been successfuly synthesized and obtained in excellent yield. Detailed UV-Vis, FT-IR and electrospray ionization mass spectroscopic data of the complexes in addition to X-ray crystallographic data of 1 which provides sufficient evidence for the formation of the complexes. The one-pot synthetic method is simple, reproducible and more convenient producing the complexes in high yield compared to previously reported methods.

Acknowledgments

Declarations

Competing Interests Statement

The authors declare no competing financial, professional, or personal interests.

Consent for publication

The authors declare that they consented to the publication of this research work.

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