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Synthesis and Crystal Structure of Novel [(u-OCH_6) (u-Cl) bis-[(bipy) (Cl)Cu(II)]]Complex

Fatima A. Ghalbuoun, Ramadan G. Abuhmaiera, Fathia A. Treish, Wedad A. Alakrash, and Ramadan M. Elmehdawi *

Chemistry Department University of Tripoli, Tripoli-Libya

Abstract: A novel title complex [(μ-chlorido)(μ-methoxido-*kO*)bis-[(2,2′-bipy-k^{2}N,N′)(chlorido) Copper(II)]] crystallizes in the monoclinic space group C2/c with unit cell parameters, a = 14.4775(2)Å, b =11.118(2)Å, c = 13.1617(2)Å, α= 90º, β=92º and γ= 90º,have two very similar distorted square-pyramidal [Cu_2(2,2′-bpy)$_2Cl_3(OCH_6)$] (1) chromophores adopting 4+1 geometrical arrangement. The u-OCH_6 and u-Cl bridges occupy a crystallographic inversion center. The novelty of this complex stems from the occupancy site (s.o.f = 0.5) of the unusual six H-atoms of the methoxy bridging group. The bridging Cl-atom occupied the axial site of the distorted square-pyramidal, which is significantly longer than the rest of the other four-basal sites. Due to axial site occupation by Cl-bridging, the two bpy-ligands lie almost perpendicular to each other. The packing structure of the title complex reveals that this structure contains inter-and intra-molecular H-bonds and ε–ε– intermolecular interactions.

Keywords: 2,2′-bipyridine; Novel complex; Square pyramidal; site occupation; Copper-complex.

1. Introduction

It is well known that bipyridine and it is analogous phenanthroline ligands are widely used in the formation of metal complexes, especially with metal ions of late first-transition series, such as Fe(II), Mn(II), Co(II), Ni(II) and Cu(II), due to robust redox stability and relative ease of functionalization and their application in catalysis, electrochemistry, and biochemistry [1-3]. Copper complexes containing bipyridine and its derivatives fascinated enormous interest due to their remarkable ε–ε-stacking interactions [4]. Due to the chelating nature of the 2,2′-bipyridine ligand, it has been used in various supramolecular architectures, especially with Cu (II) [5-8]. As also has potential antitumor activity, which is increased by coordination to Cu (II) ion. Copper (II) complexes containing 2,2-bipyridine as an ancillary ligand are antineoplastic agents which exhibit anticytotoxicity and antitumor effect. It also has been bactericidal and bacteriostatic agents for many types of bacteria. Copper (II) complexes of 2,2′-bipyridine (bpy) adopt a wide range of coordination geometries, including square pyramidal, trigonal bipyramidal, and octahedral, depending on the metal salt, type of ligand, co-ligands, counter ion, and the solvent [9]. N, N'-chelating ligand plays a vital role in tailoring the final product also, the stacking of bipyridine rings is a potential source of intermolecular exchange coupling. Due to the flexible nature of Cu(II) coordination sphere assisted by the Jahn-Teller effect, which can be realized either by distortion of an octahedral geometry to give a 4+1+1 bonding or else by changing a coordination number as an alternative means of lifting the degeneracy of unequally occupied d-orbitals so Copper will be the best choice. Herein, we report the synthesis and crystal structure of a novel Cu (II) complex.

2. Experimental section

2.1. Materials and methods

All chemicals used were of reagent grade BDH or Aldrich. All reactions were performed under atmospheric pressure. Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded at room temperature with a Bruker IFS-2 5OPUS/IR (Bruker Analytic Gmbhg, Hanau, Germany) over 400 to 4000cm^{-1} range with reflections of 4 cm^{-1}.

2.2.1. Synthesis of [(μ-chlorido) (μ-methoxido) bis-[(2,2′-bipyridine-k^{2}N, N′) (chlorido) Copper(II)]] (1)

The title complex was prepared by heating a mixture of (0.25 mmol, 0.1g) L and 2,2′-bipyridine (0.385mmol, 0.06 g) with $Cu(NO_3)_2.3H_2O$ (5.0 m mol, 0.10 g) in 20mlmethanol in the presence of Et_3N as a base. A dark brown solution was formed, and after filtration, the solution changed to a dark-green color. Prismatic green crystals suitable for

**Corresponding author:Ramadan M. Elmehdawi*
Email address: elmahdawi@yahoo.com

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X-ray analyses were obtained within two days by slow evaporation of the solvent. The title complex [Cu_2(2,2´-bpy)$_2Cl_3(OCH_6)$]. x-ray single crystal diffraction was characterized by FTIR (cm^{-1}) 3252br, 2793w, 1598w, 1470m, 1442m, 1440w, 1026w,900w, 760s, 730s.

2.2.2. Details of the Crystal Structure Determination and Refinement of Complex 1

Crystal structure data for complex (1) was collected on an Xcalibur, Atlas, Gemini ultra diffractometer equipped with a fine-focus sealed X-ray tube ($\lambda_{Cu K\alpha}$ = 1.54184 Å). Cell refinement, data collection, and reduction were undertaken via the software CrysAlisPro 1.171.41.111a [10]. Intensities were also, corrected for absorption using the same software. Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid [11]. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Using Olex2 [12], the structure was solved using SHELXT 2014/5 [13], and refined by XL [14]. Additional Cambridge Crystallographic Data Center material comprises thermal parameters and remaining bond distances and angles (CCDC No. 2178850). These data can be obtained free of charge from The Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 IEZ, UK (fax +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.UK).

Table 1. Crystal data and structure refinement of complex 1.

Empirical formula	$C_{21}H_{19}Cl_3Cu_2N_4O$
Formula weight	561.45
Temperature	150.0(2)K
Crystal system	Monoclinic
Space group	C2/c
a	14.4775(2) Å
b	11.1318(2) Å
c	13.1617(2) Å
β	92.0190(10) °
Volume	2119.83(6) $Å^3$
Z	4
$P_{calc}g/cm^3$	1.759
μ	14.646 mm^{-1}
F(000)	1136.0
Crystal size	0.22 × 0.12 × 0.11 mm^3
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.026 to 133.24
Index ranges	$-17 \leq h \leq 17$, $-13 \leq k \leq 13$, $-12 \leq l \leq 15$
Reflections collected	14652
Independent reflections	1867 [R_{int} = 0.0534, R_{sigma} = 0.0254]
Data/restraints/parameters	1867/0/143
Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0433, wR_2 = 0.1075
Final R indexes [all data]	R_1 = 0.0522, wR_2 = 0.1206
Largest diff. peak/hole / e $Å^{-3}$	0.81/-0.54

3. Results and discussion

3.1. Crystal structure of the title complex (1)

The novel title complex was synthesized by the Cu $(NO_3)_2$ reaction. $3H_2O$ with ligand "L" in presence of 2,2´-bipyridine and Et_3N as a base in methanolic solution.

Cu $(NO_3)_2.3H_2O$ + RR`R"NH^+Cl^- + 2,2´-bipyridine + Et_3N→[Cu_2 (μ-OMe)(μ-Cl)$(Cl)_2$ (2,2´- bipy$)_2$]. Where (RR'R")NH^+Cl^- as part of the ligand ("L" = $C(CH_2OH)_3N$- $(CH_2CO_2H)_2$)synthesis during the acidification process)

We really were trying to incorporate "L" as a ligand, but the high affinity of Cu (II) to bipy-ligand masked that. The crystal structure of the title complex (1) with atomic numbering scheme is presented as an ORTEP drawing (Figure 1). In contrast, its crystal packing is shown in (Figure 2a) and relevant bond distances and angles are given in (Table 2). The novel binuclear Copper (II), features two very similar distorted pyramidal CuN_2Cl_2O chromophores, both adopting a (4+1) highly distorted square-pyramidal arrangement, where t = 0.45 as described by the parameter t = (α - β)/60° (where the trans-angles α = β= 180° for perfectly square-pyramidal and α = 120° and β = 180° for perfectly triagonal-bipyramidal where β is the largest angle and α the second largest). For complexes that deviate from ideal geometries, the t-parameter will be between 0 and 1[15]. The average Cu—N bond length and the Cu—OH_2 which share two vertexes occupied by a bridging Cl-atom (source of the chloride may be due to the formation of (RR'R") NH^+ Cl^-aspart of the ligand synthesis during the acidification process), and an O-atom of a methoxy group. The bridging Cl-atom occupies one of the apical sites of the two coordination spheres of the Cu (II) polyhedron (Figure 2b). In contrast, the bridging methoxy group occupies the basal sites of both CuN_2Cl_2O square pyramids, so the Cu----Cu intermetallic distance is 3.281Å. Each Copper atom of a dimeric unit is surrounded by two nitrogen atoms from a bipyridine moiety, two Cl-atoms, and one oxygen atom of a methoxy bridge. As expected for Cu (II) ion in square-pyramidal geometry, the apical Cu1---Cl2(bridge) bond distance (2.5461Å)is significantly longer than the remaining four distances in the Cu coordination sphere, with the following distances and angles, N---Cu---N,79.65°, Cu---N1, N2 (2.019,2.058A°) and Cu---Cl (bridging)2.5461A°, Cu---Cl (terminal)2.2932A°, Cu----O,1.926A° and Cu---O---Cu,116.8°. For Cu---N and Cu---O bond lengths, all fall in the normal range [16,17]. As expected, the weak apical bond reflects a weak axial contact for Jahn-Teller sensitive Copper (II) complexes. Each N, N-chelating 2,2'-bipyridine ligand coordinates one metal ion occupying two adjacent basal sites. Consequently, both of them feature convergent nitrogen atoms and are almost perpendicular to each other due to the apical sites occupied by the bridging Cl-atom.The structure of the title complex with Cu····Cu separation of 3.281Å, which is shorter than those reported by (Elmehdawi etal[$Cu_2(C_9H_3O_6)(OH)$ $(C_{10}H_8N_2)_2].3H_2O$) [18] and (Janiac et al)[Cu_2(btb)(μ-OH)(μ-H_2O)]n [19] and longer than those reported by (Christou et al{Cu_2(μ-OH)(μ-H_2O)(μ-OAc)$(bpy)_2$] $(ClO_4)_2$) [20] and (Toki…et al [$Cu_2(phen)_2$(μ-OH) (μ-OAc)]$(NO_3)_2.H_2O$ and [$Cu_2(phen)_2(OH)$ (O_2CEt)] $(NO_3)_2.H_2O$) [21] consists of a doubly bridging pair of coordinate copper (II). The Cu---Cl apical and equatorial plane distances differ, with bond length distances of 2.5460 and 2.292A°, respectively.

Table 2. Some selected bond distances (A°) and bond angles (°) of the metal complex (1).

Cu1—Cl1	2.292(7)	Cl1—Cu1—Cl2	113.78(2)
Cu1—Cl2	2.5460(7)	Cl1—Cu1—N1	193.20(6)
Cu1—N1	2.019(2)	O1—Cu1—N1	173.05(6)
Cu1—N2	2.058(2)	N1—Cu1—N2	79.65(8)
Cu1—O1	1.9265(13)	Cu1—Cl2—Cu1	80.24(3)
Cu1—Cu1	3.281	Cu1—O1—Cl1	121.6
C11—H11(A,B,C)	0.980	Cu1—O1—Cu1	116.78(13)

The novelty of the title complex (1) lies in the site occupation by the hydrogen atoms of the methoxy group, where the site occupation factor (s.o.f) is 0.5. Further analysis of the packing structure (Figure 2c) reveals that this structure was stabilized via non-covalent intra-(C1---H····Cl1, 2.852A°; Cl1H····11A, 3.554A°; Cl1····H11B, 2.979A°; Cl1····H11C, 3.250A°; C1---H1····Cl2, 3.295A°; C1---O1····H11A, B, C, 1.960A°) and inter-molecular H-bonds and intermolecular ε–ε-interactions are found between neighboring 2,2'-bipy-molecules (Figure 2d).

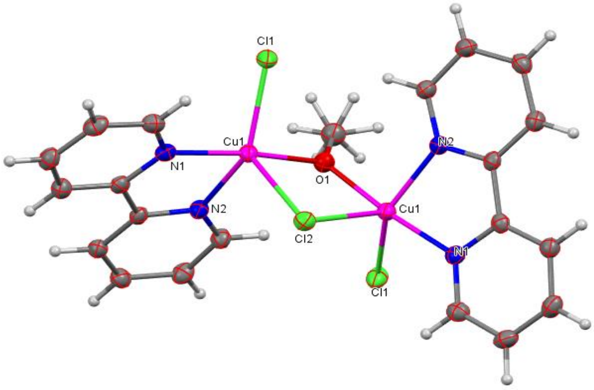

Figure 1. Crystal structure of (1). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown but not labeled

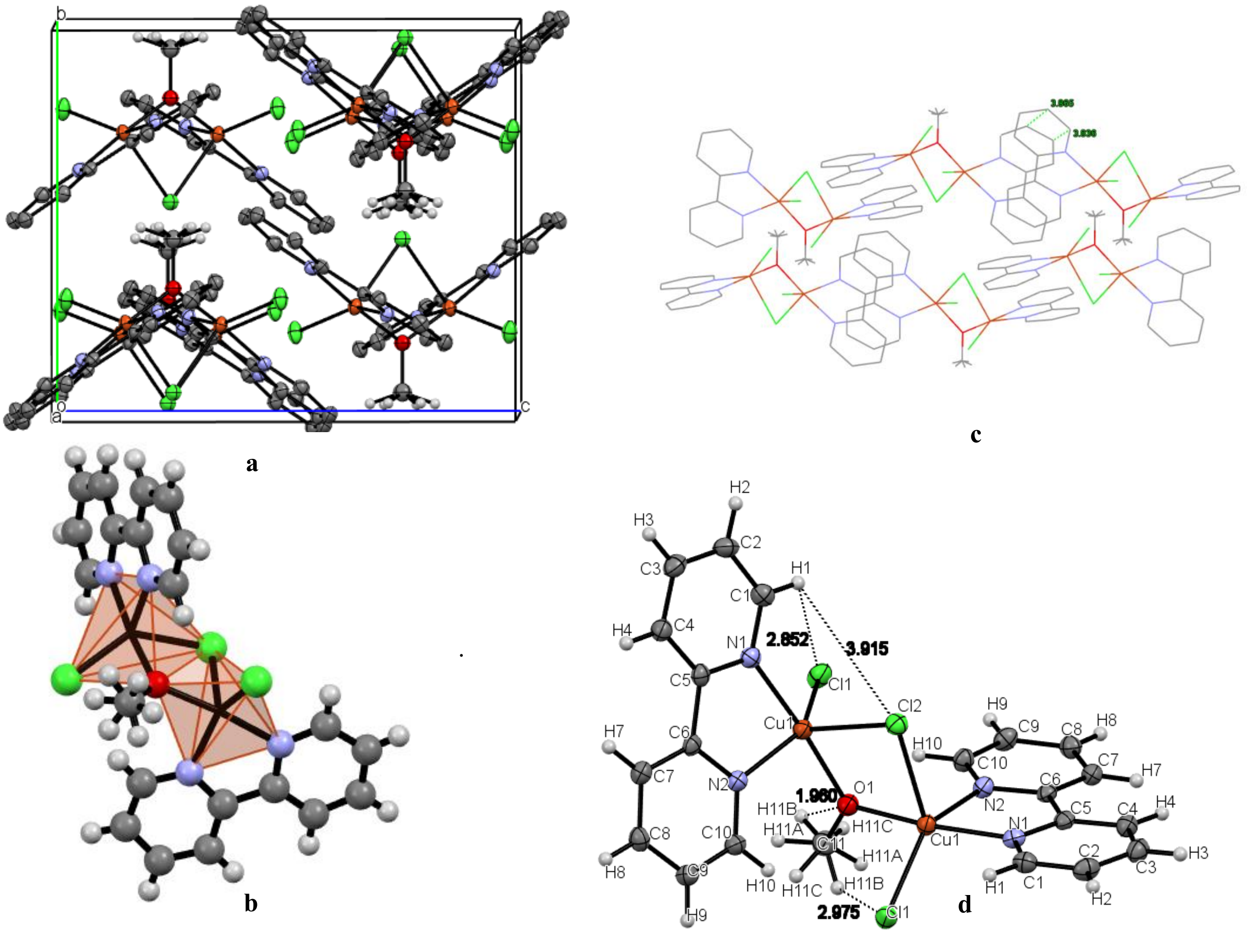

Figure 2. a: Packing structure of the title complex. **b**: Coordination polyhedron around the Cu and Na atoms. **c**: The coordination geometry and π-π-stacking around the Cu-atom. Intramolecular H-bonding. **d**: Intramolecular H-bonding. Hydrogen atoms were omitted for clarity for **a**, **b,** and **c**

4. Conclusion

A novel Cu (II) complex has been synthesized and characterized by XRD and FTIR techniques. The structure of the complex revealed distorted square-pyramidal geometry around each Cu-atom. The methoxy bridging group shows six unusual H-atoms bonded to the methoxy-carbon-atom with a site occupancy factor equal to 0.5, and all of the H-atoms are involved in H-bonding with the bridging Cl-atom and the O-atom of the methoxy bridge.

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