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Synthesis, Characterization and Crystal Structure Determination of Copper (II) Complexes with 2,2′-Dimethyl-4,4′-bithiazole

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Abstract

Copper(II) complex $[Cu(dmbt)_2(H_2O)](ClO_4)_2$ (**1**) was prepared from the reaction of copper(II) perchlorate hexahydrate with 2,2'-dimethyl-4,4'-bithiazole (dmbt) ligand in methanol at ambient temperature. The complex was quantitatively and qualitatively characterized by elemental analysis, absorption and infrared spectrometries. Complex $[Cu(DMSO)_5](ClO_4)_2$ (**2**) was also synthesized from the recrystallization of complex $[Cu(dmbt)_2(H_2O)](ClO_4)_2$ (**1**) in the dimethyl sulfoxide solvent through a slow evaporation of the solvent at room temperature. The compound was characterized by elemental analysis, infrared spectrometry and single-crystal X-ray diffraction. Crystallographic analysis of this complex revealed that the single crystal of this compound is crystallized in the trichlinic crystal structure, with the space group $P\bar{1}$ and cell dimensions of a = 10.894(3), b = 10.853(4) and c = 12.947(5)Å as well as the angle $\beta = 111.95\ (3)°$.Interestingly, this compound is the first example of 5-coordinated copper(II) complex with dimethyl-sulfoxide ligand in a square pyramid structure.

Keywords: Bithiazole ligand, Copper(II) compound, Crystal structure, DMSO.

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Introduction

There has been substantial interest in copper-based small molecules because of their relevance in the development of new reagents for catalysis, medicine and biotechnology [1-3]. Copper is one of the most abundant trace elements in biological systems and several metallo-proteins [4]. Copper(II) acts as a central key in cytochrome c, it presents unique abilities to facilitate redox reaction in bio media [5, 6]. Morover, copper (II) cations exist in the structure of many enzymes in bodies of animals. For instance Hemocyanin, Tyrosinase, and Catechol oxidases are some copper binuclear enzymes [7, 9].

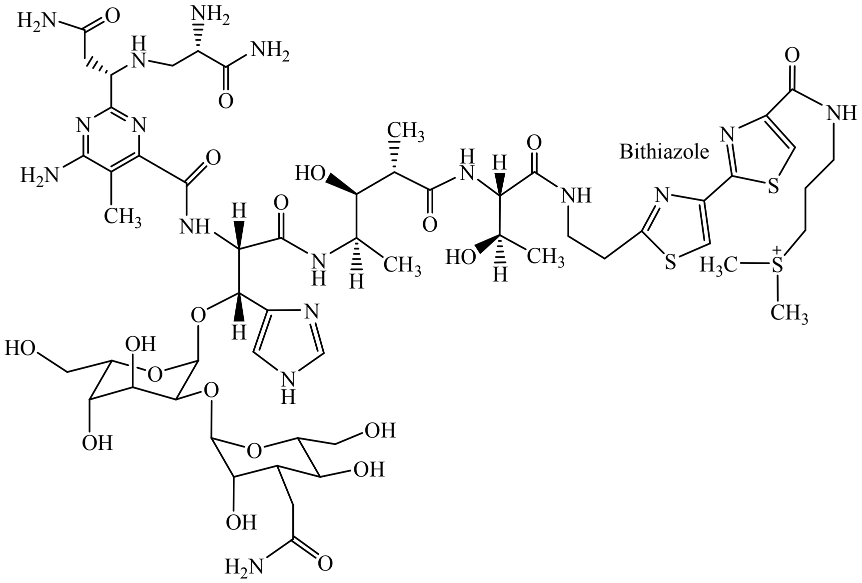
Bleomycin is an antibiotic and antitumor glycopeptide that was obtained from Streptomyces verticillus bacteria by Umezawa et al. in 1965 [10]. Today, this drug is widely used to treat head, neck and skin tumors. The molecular profile of bleomycin is shown in Scheme 1 [11]. In the structure of bleomycin there are two important domains, one for binding to the metal and another for binding to DNA. As shown in Scheme 1, the domain of bonding to the DNA consists of the bithiazole moiety and many studies have confirmed that this is where the drug interacts with DNA. As a result, bithiazole alone can be considered as a bioactive ingredient. The way bithiazole tail of the bleomycin drug binds to DNA is still in doubt.

Classical intercalation, relative stacking between alkali pairs, bonding in small cracks and insertion into a DNA spiral have been suggested for this interaction [12-14]. Due to the importance of bithiazole and its complexes, various complexes of this ligand with copper and other intermediates have been prepared by our research team and along with studying their biological and anticancer properties, their crystal structures have also been determined by X-ray diffraction [15-17].

We kept on the research to prepare complex $[Cu(dmbt)_2(H_2O)](ClO_4)_2$ (**1**). Although the proper crystal was prepared in order to determine its structure by X-ray diffraction, this complex could not be solved in chloroform, methanol, ethanol, water and acetonitrile solvents. Therefore, it was solved in dimethyl sulfoxide solvent. A suitable crystal was prepared from complex $[Cu(DMSO)_5](ClO_4)_2$ (**2**) using slow evaporation of the solvent at ambient temperature and its crystalline structure was determined by X-ray diffraction.

To date, a number of copper(II) complexes with dimethyl sulfoxide ligands have been prepared with different structures and their crystal structures were determined by X-ray diffraction, but in none of these complexes the coordination number of copper(II) cation is five and none of them had a square base pyramid structure. These complexes are: complex $[Cu(DMSO)_6](HSO_4)_2$ with slightly distorted octahedral structure [18]; complex $[Cu(DMSO)_6](I)_2.(I_2)$ with slightly distorted octahedral structure [19]; complex $[Cu(DMSO)_6](CF_3SO_3)_2$ with slightly distorted octahedral structure [20]; complex $[Cu(DMSO)_6](ClO_4)_2.2DMSO$ with slightly distorted octahedral structure [21]; complex

$[Cu(DMSO)_6][B_2(CN)_6].2DMSO$ with slightly distorted octahedral structure [22]; complex $[Cu(DMSO)_6](ClO_4)_2$ with slightly distorted octahedral structure [23]; complex $[Cu(DMSO)_6][W_6CCl_{18}]$ with slightly distorted octahedral structure [24]; and complex $[Cu(DMSO)_4][W_6CCl_{18}]_2$ with slightly distorted flat square structure [24]. As it is shown, the coordination number of copper (II) cations in none of the aforementioned complexes is five and they don't have a square pyramid structure. Thus, complex $[Cu(DMSO)_5](ClO_4)_2$ (**2**) is the first copper (II) complex with dimethyl sulfoxide ligand in which the coordination number of copper(II) cation is five and has a slightly distorted square pyramid structure.



Scheme 1. Molecular profile of bleomycin.

Experimental

Materials and instruments

In this study, 2,2'-dimethyl-4,4'-bithiazole ligand was prepared according to Ref [25]. Copper(II) perchlorate hexahydrate salt was purchased from Aldrich Company. Solvents were purchased from the Merck Company. They have been used without repurification. The absorption spectrum was recorded using DMSO solvent on Shimadzu 2100 spectrometer and infrared spectra were recorded using a CsI tablet and Shimadzu 470 spectrometer. Elemental analysis (CHSO) has been recorded and reported using the Elementar Analysis system GmbH VarioEL CHNS-O analyzer.

*Preparation of complex $[Cu(dmbt)_2(H_2O)](ClO_4)_2$ (**1**)*

2,2'-Dimethyl-4,4'-bithiazole (11.0 g, 0.56 mmol) was dissolved in 10 ml methanol and slowly added to a solution of copper(II) perchlorate hexahydrate (0.11 g, 0.28 mmol) in 10 ml methanol. A green-colored precipitation was rapidly formed. The reaction mixture was stirred at ambient temperature for 10 minutes. The resulted precipitation (**1**) was washed with acetone (yields, 0.17 g, 90.2%, m.p. 183 °C). Elemental analysis results for $C_{16}H_{18}N_4S_4CuCl_2O_9$ (with the molecular weight of 672.71) are calculated: C, 28.57; H, 2.68; S, 19.03; O, 21.41. Found: C, 28.38; H, 2.66; S, 18.89; O, 21.54. The infrared spectrum data of this complex are given in Table 1.

*Preparation of complex $[Cu(DMSO)_5](ClO_4)_2$ (**2**)*

Complex **1** (0.13 g, 0.19 mmol) was dissolved in 5 ml dimethyl sulfoxide without stirring and heating. The slow evaporation of the solvent at ambient temperature resulted in a blue cubic shaped crystals after five weeks. The complex were washed with iso-octane (yields, 0.09 g, 72.5%, m.p. 229 °C). Elemental analysis results for $C_{10}H_{30}S_5CuCl_2O_{13}$ (with the molecular weight 653.09) are calculated: C, 18.39; H, 4.59; S, 24.50; O, 31.85. Found: C: 18.27; H, 4.56; S, 24.36; O, 31.97. The infrared spectrum data of this complex are given in Table 1.

Crystal structure refinement

X-ray diffraction data for **2** was collected at 298 K by using an omega scan technique in a Bruker SMART diffraction instrument equipped with a CCD detector and a Mo K_α graphite monochromator (λ = 0.71073 Å). Data integration and correction of their numerical absorption were done using SADABS software [26]. The structure was refined by direct methods using SHELX-97 software [27]. All non-hydrogen atoms were obtained using squares of the general matrix based on F^2 with the SHELXL software as anisotropic. The function $\Sigma w(|F_o|^2=|F_c|^2)^2$ was minimized using the value of $w^{-1} = [\sigma^2(F_o)^2+(0.0399P)^2]$. In this relation, the value of P is $P=(F_o^2+2F_c^2)/3$. All hydrogen atoms were obtained as free atoms [28]. The crystal structure and packing diagram of this complex were also drawn using the Mercury software [29]. The crystalline data of **2** are given in Table 2.

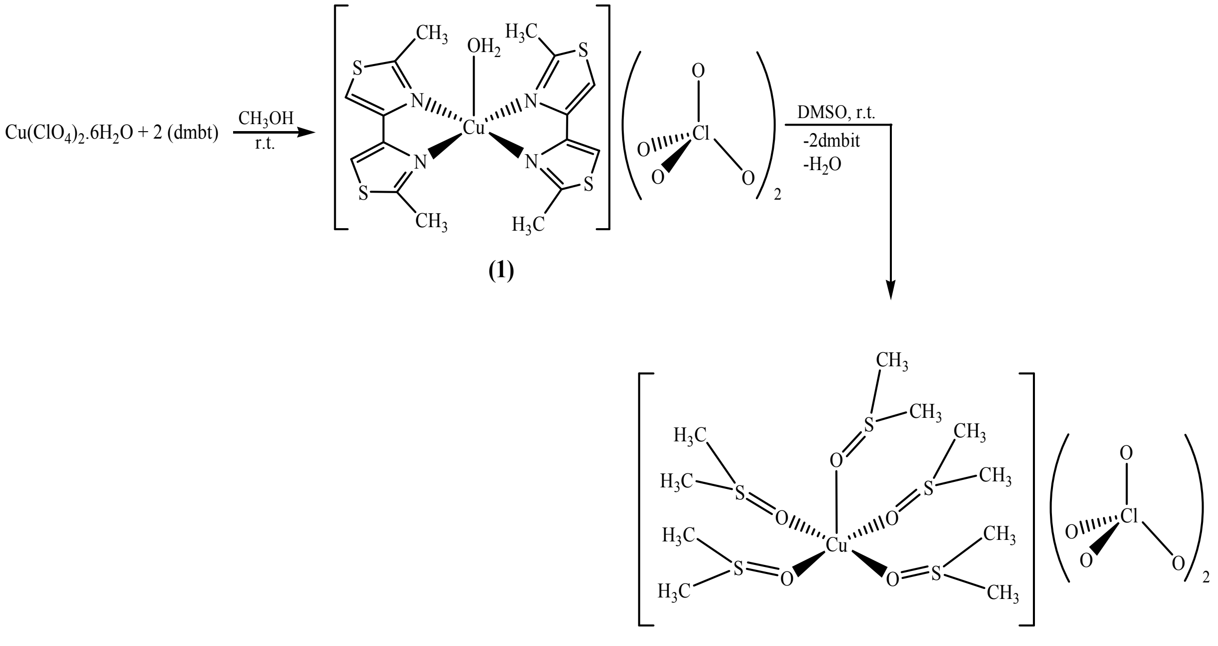
Table 1. Infrared spectra of complexes **1** and **2** and free ligands.

Compound	ν(O-H$_2$)	ν(C-H)	ν(C=C),ν(C=N), ν(C-C)	ν(C-N)	δ(C-H)	ν(Cl-O)	ν(S=O)	ν(C-S)	δ(C-S)	ν(Cu-O$_w$)	ν(Cu-O$_{DMSO}$)	ν(Cu-N)
DMSO		2996w, 2913w			1437m, 1407m	-	1050s	934m, 898m	700m, 670w	-	-	-
Dmbt		3097m, 2957w	1554m,1493s, 1417m	1237m, 1183s	1423m, 1369w	-		1066, 973m	768s, 650s, 644m	-	-	-
1	3464br	3084m, 2937w	1655s, 1532s	1296w, 1200s	1413m	1113s, 1088s		909m	764s, 600w	415m		358m
2		2994w, 2914w	-		1419m, 1403m	1116s, 1091s	986s, 950s	939s	717m, 634s, 628s	-	434m, 345m	

Result and Discussion

Synthesis of the copper (II) complexes

Complex $[Cu(dmbt)_2(H_2O)](ClO_4)_2$ (**1**) was prepared from the reaction of copper(II) perchlorate hexahydrate with 2,2'-dimethyl-4,4'-bithiazole ligand (with the ratio of 1:2) in methanol at ambient temperature. Complex $[Cu(DMSO)_5](ClO_4)_2$ (**2**) was also obtained from the re-crystallization of complex **1** in dimethyl sulfoxide (DMSO) solvent and then slow evaporation of the solvent at room temperature. As it is seen, after the re-crystallization of complex **1** in the DMSO solvent, 2,2'-dimethyl-4,4'-bithiazole ligands are replaced by DMSO, leading to complex **2**. In previous paper by our research team, after the recrystallization of complex $[In(dmbt)Cl_3(CH_3OH)].0.5dmbt$ in the DMSO solvent, the coordinated 2,2'-dimethyl-4,4'-bithiazole and methanol ligands were replaced with DMSO ligands and this led to the formation of complex $[In (DMSO)_3Cl_3]$ [30]. The elemental analysis of complexes **1** and **2** are presented in the experimental section and the infrared spectra data are given in Table 1. The complete agreement of the elemental analyses between calculated and found data of these two complexes indicates the accuracy of the proposed structure for complex **1** and the uniformity of the crystals of complex **2**. The preparation method of these two complexes is shown in Scheme 2.



Scheme 2. The preparation method of complexes **1** and **2**.

Spectroscopic characterization of $[Cu(dmbt)_2(H_2O)](ClO_4)_2$ (1)

The bands for the infrared spectra of complexes **1** and **2**, the free ligand 2,2'-dimethyl-4,4'-bithiazole and dimethyl sulfoxide are listed in Table 1. In the infrared spectra of these compounds, bands which appeared in the range of 3097 to 2913 cm^{-1} are related to the stretching vibrations of the C-H aromatic bithiazole ring and the methyl groups of dimethyl sulfoxide and bithiazole molecules [15]. The stretching vibrations of O-H water molecules, coordinated to copper(II) cation in complex complex **1** was appeared in the 3464 cm^{-1} as a slightly broad band [2, 3]. Several bands appeared in the range of 1655-600 cm^{-1} in the infrared spectra of the free dmbt ligand and complex **1** are related to the stretching vibrations of C=C, C=N, C-C, C-N and C-S, as well as the bending vibrations of C-H and C-S in the aromatic rings of the bithiazole ligand and methyl groups [2, 3, 15]. These bands are shifted to higher frequencies after the coordination of this ligand to copper(II) cation. The reason for the shift to higher frequencies is that the uncoordinated ligand has an anti structure, but becomes cis with coordination to a metal cation [2, 26]. In the infrared spectra of complexes **1** and **2**, two bands appeared in the range of 1088 to 1116 cm^{-1} which are related to the stretching vibrations of Cl-O free anion of perchlorate [31].

Two absorption bands were seen for this stretching vibration due to the difference in the length of the Cl-O bond in perchlorate anions. The lengths of the Cl-O bonds for complex **2** are shown in Table 3. Also two absorption bands were expected for the stretching vibrations S=O in complex **2** because of the existence of two types of dimethyl sulfoxide molecules coordinated to copper(II) cation that appeared in the ranges of 986 and 1950 cm^{-1}. This band has also been reported in the range of 1050 cm^{-1} for free DMSO [32].

If this molecule is coordinated from the sulfur head to metal cations, the absorption band of the stretching vibrations S=O appears in the range of 1080 to 11116 cm^{-1} while in the case of coordination from the oxygen head to the metal it appears in the range of 910 to 1000 cm^{-1}. The appearance of the stretching vibrations in the range of 950 to 986 cm^{-1} can confirm the coordination of DMSO from the oxygen head to the copper(II) cation in complex **2** [31]. The bands related to the Cu-O$_W$ and Cu-N stretching vibrations for complex **1** appear at 415 and 358 cm^{-1} respectively [2, 3]. The stretching vibrations of Cu-O$_{DMSO}$ for complex **2** also appear at 434 and 345 cm^{-1} [2, 3, 32].In the absorption spectrum of complex **1**, a band appeared at 266 nm in the DMSO solvent. An absorption band of the free ligand, 2,2'-dimethyl-4,4'-bithiazole was observed in this solvent at 265 nm, indicating the separation of 2,2'-dimethyl-4,4'-bithiazole ligands coordinated to copper(II) cation after dissolving the complex in the DMSO solvent. This absorption band is associated with the transitions of $\pi \rightarrow \pi^*$ in 2,2'-dimethyl-4,4'-bithiazole ligands [2, 3, 30].

*Crystal structure of the complex [Cu(DMSO)$_5$](ClO$_4$)$_2$ (**2**)*

Table 3 presents the bond lengths and angles and Figure 1 shows the crystal structure of complex [Cu(DMSO)$_5$](ClO$_4$)$_2$ (**2**). This complex consists of a cationic section, [Cu(DMSO)$_5$]$^{2+}$, and two anionic sections, $(ClO_4)^-$. In the cationic part of this complex, five oxygen atoms from five dimethyl sulfoxide ligands are coordinated to central copper(II) and form a square pyramid structure. The Cu-O bond length for the axial direction of this complex is 2.178(10)Å and in the square base is in the range of 1.878(13) to 1.914(15)Å.As it can be seen, the length of the Cu-O bond in the axial position is longer than the length of the Cu-O bond in the square position. The lengths of these Cu-O bonds are slightly shorter than those in complex $[Cu(DMSO)_6]^{2+}$, with a slightly distorted octahedral structure and in complex $[Cu(DMSO)_4]^{2+}$ with a slightly distorted square planar structure [24]. The bond angles in the cationic part of this complex are also in the range of 85.3 to 164.5(8)°. To determine whether a complex with a coordination number of five is in the shape of a square pyramid structure or trigonal bipyramidal structure, parameter τ is used. The value of τ is obtained from the relation $\tau = (\beta-\alpha)/60$ [32].

Table 2. Crystal data and the structural parameters of **2.**

Formula	$C_{10}H_{30}Cl_2CuO_{13}S_5$
Formula weight	653.14
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size /mm^3	0.50×0.50×0.30
a /Å	10.894(3) Å
b /Å	10.853(4) Å
c /Å	12.947(5) Å
α /°	95.83(3)°
β /°	111.95(3)°
γ /°	90.32(3)°
Volume	1410.8(9) Å^3
Z	2
Density (calc.)/g.cm^{-1}	1.537 g/cm^3
θ ranges for data collection	1.71-23.58°
F(000)	674
Absorption coefficient	1.382 mm^{-1}
Index ranges	$-11 \leq h \leq 12$ $-12 \leq k \leq 12$ $-14 \leq l \leq 13$
Data collected	7794
Unique data (R_{int})	3976, 0.0406
Parameters, restrains	290, 0
Final R_1, wR_2 (Obs. data)	0.1440, 0.1796
Final R_1,wR_2 (All data)	0.1531, 0.1970
Goodness of fit on F^2	1.250
Largest diff peak and hole/e.Å^{-3}	1.522, -1.497

The value of τ ranges from 0 for regular square pyramid complexes to 1 for trigonal bipyramidal complexes. If this value is between zero and one, the complex is tilted, depend on the amount of τ. For complex **2**, the amount of β, i.e. (O2-Cu1-O4), is 164.5(8)° and the amount of α, i.e. (O3-Cu1-O5), is 163.3(8)°. Therefore, the τ value for this complex is 0.02 which indicates that the structure of this complex is quit slightly distorted from a regular square pyramid. The length of the Cl-O bond in perchlorate anions was also in the range of 1.183(5) to 1.402(4)Å. The lengths of these bonds are slightly shorter than the anion perchlorate in complex $[Cu(bip)(DMSO)_4](ClO_4)_2$ with a slightly distorted octahedral structure [33]. Table 4 presents lengths and angles of the hydrogen bonds and Figure 2 shows the packing diagram of complex **2** in the unit cell. In this complex, the intermolecular C-H...O hydrogen bonds between the oxygen atoms of perchlorate anions and the hydrogen atoms of methyl groups of dimethyl sulfoxide ligands stabilized the crystal structure of this complex.

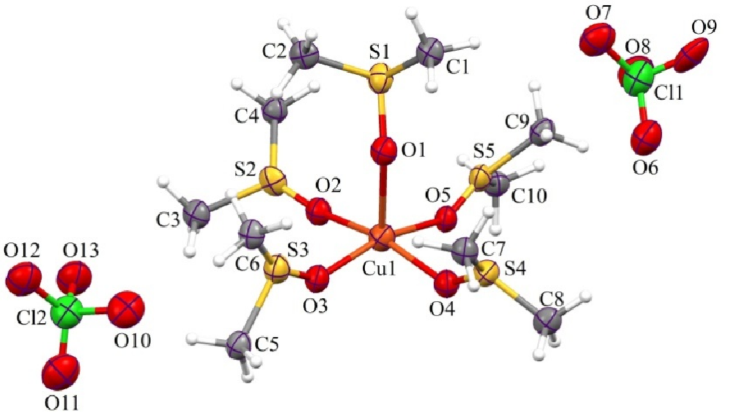


Figure 1. The molecular structure of **2**, with the atom numbering scheme.

Table 3. Selected bond lengths (Å) and angles (º) for **2**.

Cu1-O1	2.178(10)	Cl2-O11	1.233(4)
Cu1-O2	1.878(13)	O3-Cu1-O4	87.9(13)
Cu1-O3	1.903(12)	O3-Cu1-O2	92.3(14)
Cu1-O4	1.906(16)	O4-Cu1-O2	164.5(8)
Cu1-O5	1.914(15)	O3-Cu1-O5	163.3(8)
Cl1-O7	1.396(4)	O4-Cu1-O5	90.0(13)
Cl1-O8	1.224(5)	O2-Cu1-O5	85.3(15)
Cl1-O9	1.183(5)	O3-Cu1-O1	92.1(8)
Cl1-O6	1.271(4)	O4-Cu1-O1	93.8(6)
Cl2-O10	1.353(2)	O2-Cu1-O1	101.7(8)
Cl2-O12	1.402(4)	O5-Cu1-O1	104.5(7)
Cl2-O13	1.330(5)		

Table 4. Hydrogen bond geometry for **2** in crystal packing.

D-H…A	D-H (Å)	H…A (Å)	D…A (Å)	D-H…A (Å)	Symmetry code
C2 -H2B...O9	0.95	2.53	3.21(6)	129	-
C4-H4A...O10	0.96	2.55	3.45(4)	155	-x+1,-y+1,-z+1
C6-H6C...O10	0.96	2.48	3.43(8)	169	-x+2,-y+1,-z+1
C9-H9A...O12	0.96	2.24	3.19(6)	172	-x+1,-y+2,-z+1
C10-H10A...O11	0.96	2.53	3.29(7)	137	x-1,+y,+z

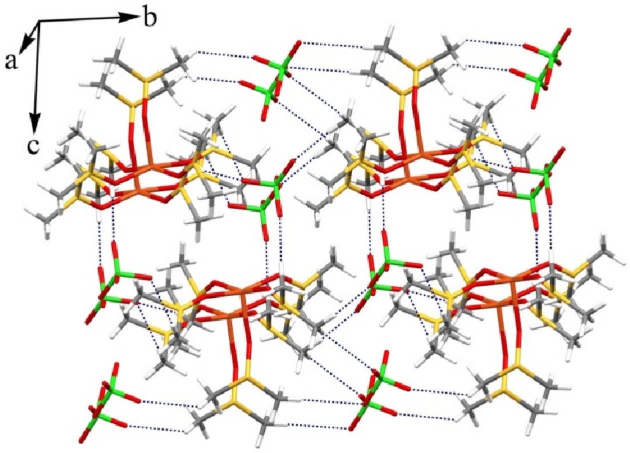


Figure 2. The unit cell packing diagram of **2**. Hydrogen bonds C-H...O are specified with dashed lines.

Conclusion

In this research, two new copper(II) complexes [Cu(dmbt)$_2$(H$_2$O)](ClO$_4$)$_2$ (**1**) and [Cu(DMSO)$_5$](ClO$_4$)$_2$ (**2**) were prepared and characterized. The pharmacological investigation on title compounds are necessary and worthwhile, because similar copper(II) compounds illustrated bioactivity such as DNA interaction and antitumor potency.

Supplementary Information

Complex **2** has been registered with the number 643397 at the Cambridge Crystal Data Center (CCDC). Structural complementary information for this complex is available at www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment

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