Synthesis, Characterization and Crystal Structures of Mixed-Ligand Complexes of $[Cu(bipy)_2N_3(ClO_4)]$ and $[Cu(5,5'\text{-}DiMebipy)_2(N_3)](ClO_4)$

Oluwafunmilayo Florence Adekunle[1,2,*], Ray John Butcher[1], Oladapo Bakare[1],
Joseph Anthony Orighomisan Woods[3], and Olusegun Ayobami Odunola[4]

[1]*Department of Chemistry, Howard University, 525 College Street, Washington DC, USA*

[2]*Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology*
P.M.B.4000, Ogbomoso, Oyo-State, Nigeria

[3]*Department of Chemistry, University of Ibadan, Ibadan, Oyo-State, Nigeria*

[4]*Department of Chemistry, Hallmark University, Ijebu-Itele, Ogun-State, Nigeria*

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ABSTRACT

Two mixed –ligand complexes $[Cu(bipy)_2N_3(ClO_4)]$ and $[Cu(5,5'\text{-}DiMebipy)_2(N_3)](ClO_4)$ have been prepared and characterized. The compounds were characterized by elemental analyses, IR and UV-Visible spectroscopy, room temperature magnetic susceptibility measurements, and conductivity measurement, while the solid-state structures have been established by single-crystal X-ray diffraction analyses. $[Cu(bipy)_2N_3(ClO_4)]$crystallizes in the monoclinic space group $P2_1/c$ with cell constants a = 16.9027(3) Å, b = 7.59087(9) Å, c = 17.2614(3) Å, β = 111.2808(19)° and Z = 4. $[Cu(5,5'\text{-}DiMebipy)_2(N_3)](ClO_4)$ also crystallizes in the monoclinic space group $P2_1/c$ with the cell constants a = 16.0312(11) Å, b = 7.9889(5) Å, c = 20.7167(18) Å, β = 110.285(8)° and Z = 4. The UV-Vis spectra and X-ray determination indicate that $[Cu(bipy)_2N_3(OClO_3)]$ is distorted octahedral ligand field and non-electrolyte in nature while $[Cu(5,5'\text{-}DiMebipy)_2(N_3)](ClO_4)$ is a square pyramidal five coordinate complex and a 1:1 electrolyte. The magnetic moments of the two complexes in the range 1.78–1.83 B.M. reveal a single unpaired electron with a slight orbital contribution.

***Keywords**: monoclinic; electronic spectra; electrolyte; 2,2'-bipyridyl; X-ray structure*

ABSTRAK

Dua senyawa kompleks dengan ligan campuran $[Cu(bipy)_2N_3(ClO_4)]$ dan $[Cu(5,5'\text{-}DiMebipy)_2(N_3)](ClO_4)$ telah dipreparasi dan dikarakterisasi. Senyawa dikarakterisasi dengan analisis unsur, spektroskopi IR dan UV-Visibel, pengukuran suseptibilitas magnetik temperatur kamar, dan konduktivitas, sedangkan struktur zat-padat ditetapkan dengan analisis difraksi sinar-x kristal tunggal. $[Cu(bipy)_2N_3(ClO_4)]$ mengkristal dalam kelompok ruang monoklinik $P2_1/c$ dengan tetapan sel a = 16,9027(3) Å, b = 7,59087(9) Å, c = 17,261di4(3) Å, β = 111,2808(19)° dan Z = 4. $[Cu(5,5'\text{-}DiMebipy)_2(N_3)](ClO_4)$ juga mengkristal dalam kelompok ruang yang sama dengan tetapan sel a = 16,0312(11) Å, b = 7,9889(5) Å, c = 20,7167(18) Å, β = 110,285(8)° and Z = 4. Spektra UV-Vis spektra dan penentuan X-ray mengindikasikan bahwa $[Cu(bipy)_2N_3(OClO_3)]$ merupakan kompleks medan oktahedral terdistorsi dan non-elektrolit di alam sedangkan $[Cu(5,5'\text{-}DiMebipy)_2(N_3)](ClO_4)$ merupakan kompleks koordinat lima piramida segiempat dan elektrolit 1:1. Momen magnetik dua senyawa complexes dalam kisaran 1,78–1,83 B.M. menunjukkan terdapat electron tunggal tidak berpasangan dengan kontribusi orbital sedikit.

***Kata Kunci**: monoklinik; spektra elektronik; elektrolit; 2,2'-bipyridyl; struktur sinar-x*

INTRODUCTION

The developments in the field of coordination chemistry which is closely bound to the study of mixed-ligand complexes have attracted a lot of interest in recent years. This is due to the various pharmacological effects of the mixed-ligand complexes, their anti-microbial, catalytic, anti-cancer, potential applications in nanoscience and also in enzyme inhibition [1-2]. The formation of mixed-ligand complexes containing organic and inorganic ligands sometimes determines the mechanism of the analytical reaction and the composition of the end product [3].

Metal complexes of 1,10-phenanthroline,2,2'-bipyridine and their derivatives have been of tremendous interest to coordination chemists mainly due

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[*] Corresponding author.
Email address : fnnmy2001@yahoo.com

Table 1. Crystal data and structure refinement for [Cu(bipy)$_2$ N$_3$(OClO$_3$)] (**1**) and [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) (**2**)

	1	**2**
Empirical formula	C_{20} H_{16} Cl Cu N_7 O_4	C_{24} H_{24} Cl Cu N_7 O_4
CCDC Number	1418813	1471688
Temperature	120(2) K	173(2) K
Wavelength	1.54184 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 21/c	P21/c
Unit cell dimensions		
a	16.9027(3) Å	16.0312(11) Å
b	7.59087(9) Å	7.9889(5) Å
c	17.2614(3) Å	20.7167(18) Å
α	90°	90°
β	111.2808(19)°	110.285(8)°
γ	90°.	90°
Z	4	4
Absorption coefficient	3.091 mm^{-1}	1.031 mm^{-1}
F(000)	1052	1180
Crystal size	0.39 x 0.18 x 0.16 mm^3	0.29 x 0.17 x 0.10 mm^3
Independent reflections	4255 [R(int) = 0.0214]	8503 [R(int) = 0.0539]
Completeness to theta = 67.50°	99.90%	99.70%
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.62061	1.00000 and 0.54600
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.052	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0291, wR2 = 0.0794	R1 = 0.0481, wR2 = 0.1054
R indices (all data)	R1 = 0.0301, wR2 = 0.0801	R1 = 0.0851, wR2 = 0.1255
Extinction coefficient	0.00098(12)	N/a
Largest diff. peak and hole	0.354 and -0.509 e.Å^{-3}	0.474 and -0.704 e.Å^{-3}

to their stability in biochemical processes [4] and in the study of interaction of DNA and proteins [5]. It is well known that copper(II) ion can form numerous bis-bipyridine complexes [6-10].

Mixed ligand complexes are known for their extreme stability and the display of chemical individuality of the central atom [3]. A number of factors that are responsible for the composition and stability of mixed ligand complexes include the electronic structure of the central metal atom and its coordination number, the donor nature of ligands and mutual effect of ligands in a mixed ligand complex, the geometric structure of the complex and the coordination equilibria in solutions of the complexes [3].

The coordination chemistry of ambidentate ligands possessing two different atoms such as SCN$^-$, NO$_2^-$, N$_3^-$, Cl$^-$ etc capable of coordinating to metal ions has been a subject of interest to both synthetic and theoretical coordination chemists for a long time [11-17].

The interest in the azide ligand is as a result of its different coordination which could be end-on, end –to – end and so on [18].

The present paper reports the synthesis, characterization and X-ray structures of the mixed ligand complexes [Cu(bipy)$_2$N$_3$(OClO$_3$)] (**1**) and [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) (**2**) obtained by the reaction between Cu(bipy)$_2$(ClO$_4$)$_2$, Cu(5,5'-DiMebipy)$_2$(ClO$_4$)$_2$ and sodium azide respectively.

EXPERIMENTAL SECTION

Materials

The ligand 2,2'-bipyridine, copper perchlorate hexahydrate, sodium azide and other reagents were purchased from Aldrich Chemical Co., Burgoyne Burbidges & Co (India) and were used without further purification. Bis-(2,2'-bipyridine)copper perchlorate, Cu(bipy)$_2$(ClO$_4$)$_2$ and bis-(5,5'-dimethyl-2,2'-bipyridine) copper perchlorate, Cu(5,5'-DiMebipy)$_2$(ClO$_4$)$_2$ were synthesized according to published procedures [6-7].

Perchlorates are potentially explosive. So also are azido compounds especially in the presence of organic ligands [19]. Only a small amount of these materials should be prepared and handled with care.

Procedure

Physical measurements

CHN analyses were carried out by Atlantic Microlab, Atlanta GA. Electronic spectra were recorded on a Unicam Helios γ-Spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer PE 100 spectrometer with an Attenuated Total Reflectance (ATR) window. The room temperature magnetic susceptibilities were recorded using Sherwood Scientific magnetic susceptibility balance MSB MK1. Susceptibilities were corrected considering the sample holder as the background and the diamagnetic contribution calculated from Pascal constants. Conductance measurements of *ca*. 10^{-3} M solutions of the complexes in CH_3CN were measured using a Jenway 4310 Conductivity meter.

X-ray diffraction analysis

Single crystals of both complexes were obtained by the slow evaporation of the acetonitrile solutions of the compounds. Single-crystal X-ray diffraction data for **1** was collected on an Oxford Diffraction (now Agilent) Gemini-R diffractometer while diffraction data for **2** was collected on a Bruker Quest diffractometer. For **1** cell refinement data collection and processing was carried out using CrysAlis Pro [20] while for **2** cell refinement data collection and processing was carried out using Apex 2 software [21]. Both structures were solved and refined using the SHELXTL suite of programs [22].

Synthesis of [Cu(bipy)$_2$N$_3$(OClO$_3$) (1)

To a solution of the complex [Cu(bipy)$_2$](ClO$_4$)$_2$ (1.6 mmol, 0.92 g) in acetonitrile (100 mL) was added 0.8 mmol (0.052 g) of sodium azide and the reaction was mixture stirred for 24 h. The deep green solution obtained was left on the bench for 5 days for crystallization by slow evaporation; the green crystalline compound obtained was filtered off by suction, washed with CH_3CN, and dried in air. Single crystals suitable for X-ray diffraction experiment were obtained from acetone/n-hexane solution of the complex. Anal. Calcd for [Cu(bipy)$_2$N$_3$(OClO$_3$)](%) C, 46.44; H, 3.19; N, 18.82. Found: C, 46.39; H, 3.14; N, 18.86.Yield: 0.8282g (92%).

Synthesis of [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) (2)

Sodium azide (7.2 mmol, 0.47g) was added to a solution Cu(5,5'-DiMebipy)$_2$(ClO$_4$)$_2$ (0.8 mmol, 0.51g) in 50 mL distilled water and the mixture was boiled under

Table 2. Selected Bond Lengths (Å) and angles (°) for [Cu(bipy)$_2$ N$_3$(OClO$_3$)] (**1**) and [Cu(5,5'-DiMebipy)$_2$(N$_3$)] (ClO$_4$) (**2**)

	1	**2**
Cu-N1 (N1A)	2.0030(14)	2.0005(18)
Cu-N2 (N2A)	2.0353(14)	2.0460(18)
Cu-N3 (N1B)	2.2066(14)	1.9926(18)
Cu-N4 (N2B)	2.0140(13)	2.1795(18)
Cu-N11	1.9848(15)	1.973(2)
Cu-O2	2.8511(13)	N/a
N1-Cu-N2	80.68(6)	80.46(7)
N1-Cu-N3 (N1B)	108.58(5)	172.41(7)
N1-Cu-N4 (N2B)	172.75(5)	105.34(7)
N1-Cu-N11	91.87(6)	91.99(8)
N1-Cu-O2	93.09(5)	N/a
N2-Cu-N3 (N1B)	90.08(5)	93.50(7)
N2-Cu-N4 (N2B)	96.96(5)	92.02(7)
N2-Cu-N11	165.08(6)	161.74(9)
N2-Cu-O2	75.58(5)	N/a
N3 (N1B)-Cu-N4 (N2B)	78.17(5)	79.30(7)
N3 (N1B)-Cu-N11	104.59(6)	92.45(8)
N3 (N1B)-Cu-O2	162.30(4)	N/a
N4 (N2B)-Cu-N11	88.84(6)	106.05(8)
N4 (N2B)-Cu-O2	93.09(5)	N/a
N(13)-N(12)-N(11)	176.61(18)	176.7(3)

Table 3. Hydrogen bonds for [Cu(bipy)$_2$ N$_3$(OClO$_3$)] (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(9A)-H(9AA)...O(2)#1	0.95	2.49	3.388(2)	158.7
C(8B)-H(8BA)...O(3)#2	0.95	2.43	3.317(2)	155.7
C(3A)-H(3AA)...O(4)#3	0.95	2.55	3.324(2)	139.3
C(7A)-H(7AA)...O(1)#4	0.95	2.36	3.305(2)	172.3

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z #2 -x+1,y-1/2,-z+1/2 #3 -x+2,-y+2,-z+1
#4 -x+2,-y+1,-z+1

and [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1AA)...N(11)	0.95	2.47	2.984(3)	114.2
C(5)-H(5AA)...O(1A)#1	0.95	2.57	3.343(13)	138.6
C(8)-H(8AA)...O(3)#1	0.95	2.41	3.354(3)	171.7
C(8)-H(8AA)...O(1A)#1	0.95	2.61	3.474(15)	151.8
C(12)-H(12A)...N(3)	0.95	2.58	3.114(3)	116.2
C(13)-H(13A)...O(2)#2	0.95	2.51	3.442(4)	165.7
C(17)-H(17A)...N(11)#3	0.95	2.65	3.534(3)	154.5
C(24)-H(24A)...O(4A)	0.95	2.54	3.38(2)	146.9

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y-1/2,-z+1/2 #2 x,-y+1/2,z-1/2 #3 -x,-y,-z

Table 4. Selected Infrared spectral data of the complexes (cm^{-1})

Complex	Ring v(C=N)	v$_{as}$(N$_3$)	v$_s$(N$_3$)	perclorate v(Cl-O)	Water v(O-H)	v(Cu-N)	v(Cu-O)
[Cu(bipy)$_2$ N$_3$(OClO$_3$)]	1568	2038	1318	1090,773	3439	623	420
[Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$)	1574	2035	1319	1094,833	3453	621	-

reflux for 2 h. The deep-green micro-crystalline compound obtained was filtered by suction, washed with distilled water and dried in the air. The crude compound was recrystallized from distilled water. Crystals suitable for X-ray analysis were obtained from the compound. Anal. Calcd for [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) (%)C, 50.24; H, 4.22; N, 17.10. Found: C, 49.97; H, 4.05; N, 17.15. Yield: 0.279g (60%).

RESULT AND DISCUSSION

Synthesis and Characterization

The complexes [Cu(bipy)$_2$N$_3$(OClO$_3$) (**1**) and [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) (**2**) are air-stable, moisture-insensitive compounds and crystalline. The Microanalytical data (C, H and N) gave satisfactory results which are useful to formulate the complexes. The compounds were obtained in good yield.

Infrared Spectra

The Infrared spectral of both complexes confirm the presence of the azido group and each complex exhibits the v$_{as}$(N$_3$) band at 2028 cm^{-1} and 2035 cm^{-1} respectively for (**1**) and (**2**) and the v$_s$(N$_3$) band at 1318 cm^{-1} and 1319 cm^{-1} respectively Fig. 5 and Fig. 6.

This confirms the coordination of the azide ligands to the copper atom [24-28]. The complexes exhibit the asymmetric Cl-O stretching mode of the perchlorate anion at 1051 cm^{-1} and 1094 cm^{-1} and the asymmetric bending mode at 765 cm^{-1} and 833 cm^{-1} for complexes (**1**) and (**2**) respectively (Table 4) [26,29-31]. The v(C=N) of the ring was observed at 1568 cm^{-1} (**1**) and 1574 cm^{-1} (**2**) [32-33]. The presence of water molecules in the crystal lattice was revealed by the bands at 3439 cm^{-1} and 3453 cm^{-1} respectively for the complexes [34-35]. The coordination of the azide ligand and the perchlorate anion to complex (**1**) is supported by the bands observed at 623 cm^{-1} and 420 cm^{-1} respectively for the v(Cu-N) and v(Cu-O) which is similar to reported systems [36-42].

Electronic Spectra

The UV-visible spectra of the complexes (**1**) and (**2**) (Table 5) in CH$_3$CN solution show one broad absorption band each centered at 13986 cm^{-1} and 14205 cm^{-1} respectively (Fig. 7 and Fig. 8). This broad band in complex (**1**) is assignable to the $^2T_{2g} \leftarrow {}^2E_{2g}$ transition in an octahedral geometry [26,37,43-48] while in (**2**) it is attributed to the high –energy, high intensity peak $d_{xz} = d_{yz} \rightarrow d_{x2-y2}$ transition for a square pyramidal geometry [12,27,49-56]. The broadness in the observed bands may be attributed to a Jahn-Teller distortion of these geometries [26]. The ligand based transitions for these complexes attributed to π → π* were observed around 32468–43860cm^{-1} while an additional band at 23148cm^{-1} exhibited by complex (**1**)

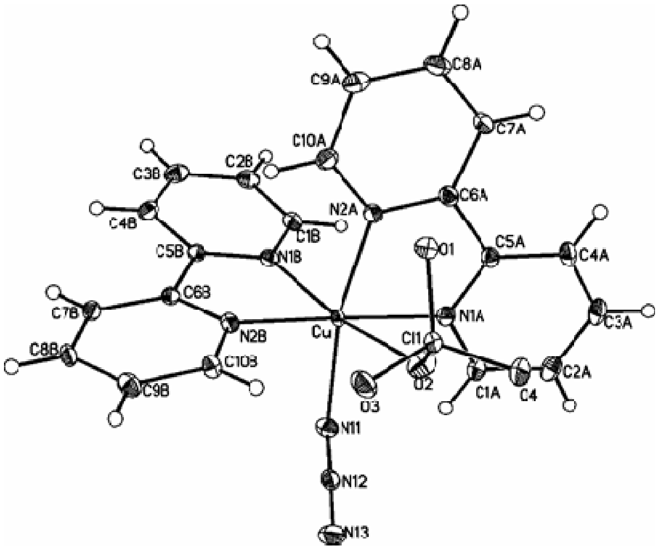

Fig 1. Molecular diagram for [Cu(bipy)$_2$N$_3$(OClO$_3$)] showing atom labeling. ADP's at the 30% probability level

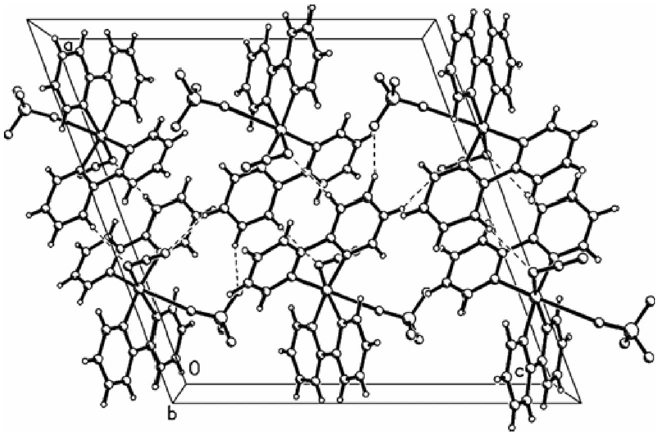

Fig 2. Packing for [Cu(bipy)$_2$N$_3$(OClO$_3$)] viewed along the *b* axis

Table 5. Electronic absorption values, μ_{eff} and conductivity data of the complexes

Compound	Intraligand and d-d transitions, λ_{max} (cm^{-1})	Geometry	μ_{ef} (B.M.)	Λ_M(mho cm^2 mol-1)
[Cu(bipy)$_2$ N$_3$(OClO$_3$)]	33223, 23148, 13986	Distorted octahedral	1.78	17
[Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$)	43860, 39370, 32468, 24631, 14205	Distorted square pyramidal	1.83	131

Table 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for [Cu(bipy)$_2$ N$_3$(OClO$_3$)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Cu	7210(1)	6159(1)	5204(1)	15(1)
Cl(1)	8037(1)	7127(1)	3300(1)	18(1)
O(1)	8401(1)	5381(2)	3429(1)	25(1)
O(2)	7820(1)	7627(2)	4006(1)	29(1)
O(3)	7282(1)	7128(2)	2563(1)	28(1)
O(4)	8642(1)	8369(2)	3207(1)	30(1)
N(11)	6529(1)	8312(2)	5160(1)	23(1)
N(12)	6346(1)	9248(2)	4562(1)	21(1)
N(13)	6145(1)	10203(2)	3999(1)	32(1)
N(1A)	8274(1)	7327(2)	5957(1)	18(1)
N(2A)	8078(1)	4379(2)	5124(1)	17(1)
C(1A)	8304(1)	8865(2)	6343(1)	22(1)
C(2A)	9067(1)	9702(2)	6776(1)	27(1)
C(3A)	9816(1)	8928(3)	6805(1)	28(1)
C(4A)	9788(1)	7317(2)	6413(1)	24(1)
C(5A)	9003(1)	6541(2)	5994(1)	18(1)
C(6A)	8892(1)	4831(2)	5559(1)	18(1)
C(7A)	9563(1)	3739(2)	5596(1)	26(1)
C(8A)	9384(1)	2157(2)	5167(1)	29(1)
C(9A)	8554(1)	1696(2)	4717(1)	27(1)
C(10A)	7915(1)	2849(2)	4715(1)	21(1)
N(1B)	6784(1)	4267(2)	5942(1)	18(1)
N(2B)	6187(1)	5073(2)	4329(1)	17(1)
C(1B)	7179(1)	3769(2)	6733(1)	22(1)
C(2B)	6916(1)	2337(2)	7077(1)	27(1)
C(3B)	6206(1)	1408(2)	6584(1)	27(1)
C(4B)	5782(1)	1932(2)	5769(1)	22(1)
C(5B)	6096(1)	3359(2)	5464(1)	17(1)
C(6B)	5710(1)	3957(2)	4585(1)	16(1)
C(7B)	4909(1)	3429(2)	4052(1)	20(1)
C(8B)	4606(1)	4044(2)	3239(1)	21(1)
C(9B)	5103(1)	5169(2)	2977(1)	23(1)
C(10B)	5891(1)	5659(2)	3541(1)	21(1)

is due to charge transfer (CT) [27,34].

Conductivity

The molar conductance data in acetonitrile at room temperature [Table 5] supported the crystallographic elucidation of the structure of [Cu(bipy)$_2$N$_3$(OClO$_3$)] (**1**) which is a non-electrolyte and carried no counter ion while (**2**) with a perchlorate counter ion on the other hand is a 1:1 electrolyte [39, 57]. This observation corroborates the coordination of the perchlorate anion in (**1**) to the Cu atom Fig.1 and Fig. 2, which in (**2**) is not observed in the coordination sphere Fig. 3.

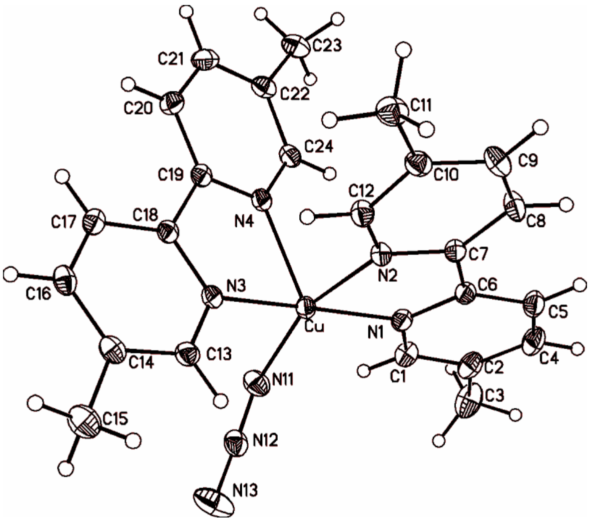

Fig 3. Molecular diagram for [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$)

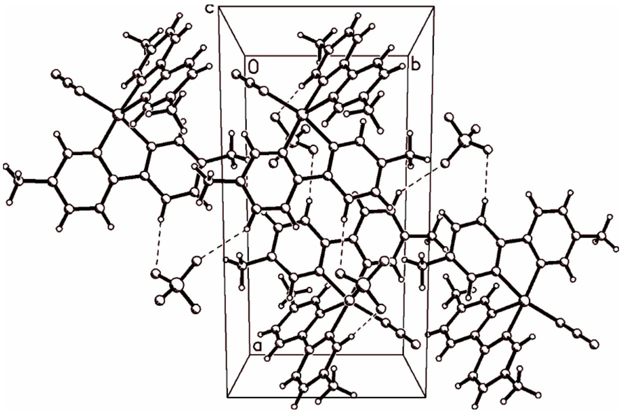

Fig 4. Packing diagram for [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) viewed along c-axis

Magnetic Moment

The magnetic susceptibility measurements of the complexes reveal that the Cu(**II**) complexes are paramagnetic, corresponding to the +2 state of copper in the complexes. The moments 1.78–1.83 B.M. are slightly higher than expected for the spin only value of one unpaired electron (1.73B.M.) which is as a result of

Table 7. Anisotropic displacement parameters (Å^{2}x 10^3) for [Cu(bipy)$_2$ N$_3$(OClO$_3$)]. The anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}

	U11	U22	U33	U23	U13	U12
Cu	12(1)	16(1)	17(1)	-1(1)	3(1)	-1(1)
Cl(1)	15(1)	18(1)	20(1)	0(1)	5(1)	-1(1)
O(1)	21(1)	19(1)	33(1)	2(1)	7(1)	4(1)
O(2)	41(1)	25(1)	26(1)	-4(1)	18(1)	-1(1)
O(3)	18(1)	33(1)	25(1)	0(1)	0(1)	2(1)
O(4)	22(1)	27(1)	41(1)	6(1)	12(1)	-5(1)
N(11)	22(1)	22(1)	25(1)	0(1)	8(1)	5(1)
N(12)	14(1)	19(1)	26(1)	-6(1)	4(1)	0(1)
N(13)	36(1)	24(1)	28(1)	3(1)	3(1)	7(1)
N(1A)	17(1)	20(1)	16(1)	0(1)	5(1)	-2(1)
N(2A)	15(1)	18(1)	18(1)	1(1)	6(1)	0(1)
C(1A)	24(1)	23(1)	19(1)	-4(1)	8(1)	-4(1)
C(2A)	33(1)	25(1)	22(1)	-6(1)	9(1)	-10(1)
C(3A)	24(1)	33(1)	23(1)	-2(1)	4(1)	-14(1)
C(4A)	16(1)	30(1)	22(1)	3(1)	4(1)	-4(1)
C(5A)	16(1)	21(1)	16(1)	2(1)	4(1)	-2(1)
C(6A)	16(1)	20(1)	19(1)	3(1)	6(1)	1(1)
C(7A)	18(1)	27(1)	31(1)	4(1)	7(1)	4(1)
C(8A)	29(1)	24(1)	38(1)	4(1)	16(1)	10(1)
C(9A)	34(1)	19(1)	30(1)	-1(1)	15(1)	3(1)
C(10A)	23(1)	18(1)	23(1)	-1(1)	8(1)	-1(1)
N(1B)	16(1)	18(1)	19(1)	0(1)	7(1)	2(1)
N(2B)	13(1)	20(1)	18(1)	-1(1)	5(1)	0(1)
C(1B)	21(1)	25(1)	20(1)	0(1)	6(1)	3(1)
C(2B)	30(1)	27(1)	23(1)	6(1)	10(1)	7(1)
C(3B)	35(1)	21(1)	31(1)	5(1)	18(1)	2(1)
C(4B)	24(1)	17(1)	27(1)	-2(1)	13(1)	-1(1)
C(5B)	16(1)	16(1)	20(1)	-2(1)	8(1)	2(1)
C(6B)	15(1)	15(1)	20(1)	-3(1)	7(1)	1(1)
C(7B)	16(1)	18(1)	25(1)	-5(1)	8(1)	-1(1)
C(8B)	14(1)	25(1)	22(1)	-9(1)	3(1)	1(1)
C(9B)	19(1)	28(1)	18(1)	-2(1)	4(1)	3(1)
C(10B)	17(1)	26(1)	18(1)	1(1)	6(1)	0(1)

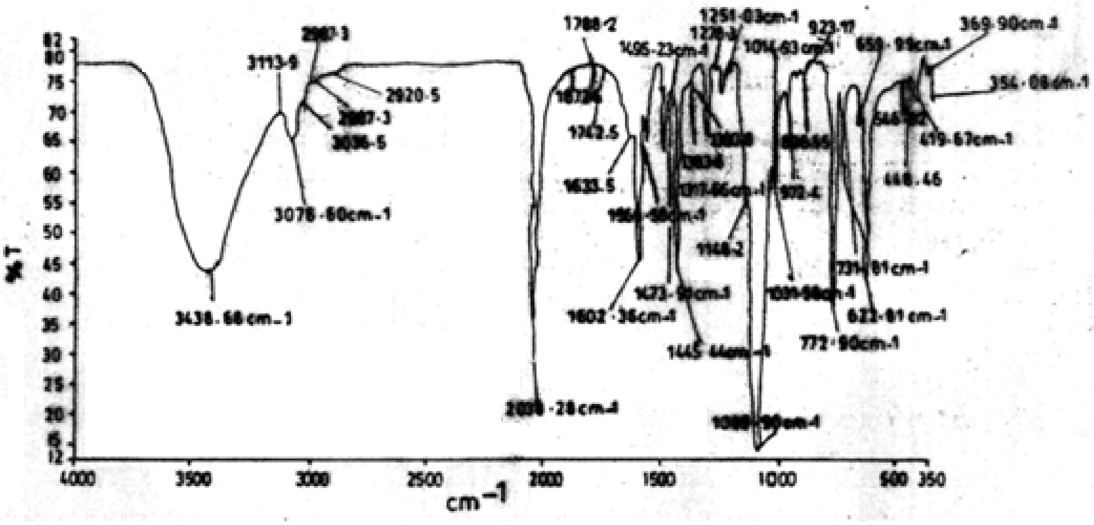

Fig 5. Infrared spectra of [Cu(bipy)$_2$N$_3$(OClO$_3$)] (**1**)

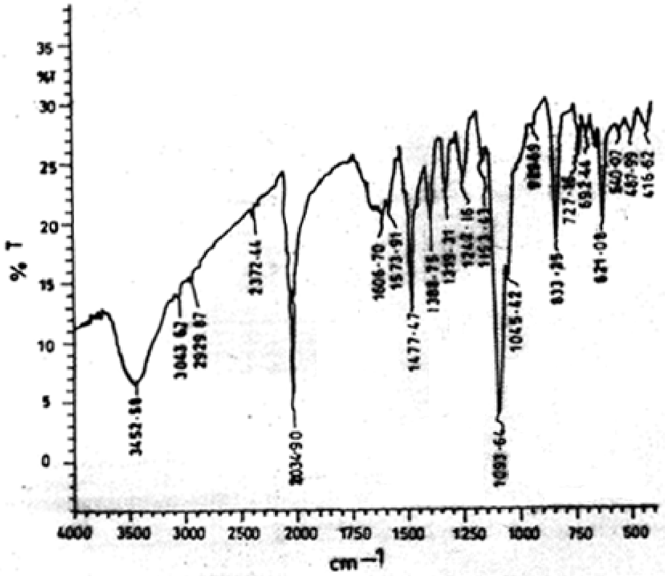

Fig 6. Infrared spectra of [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) (**2**)

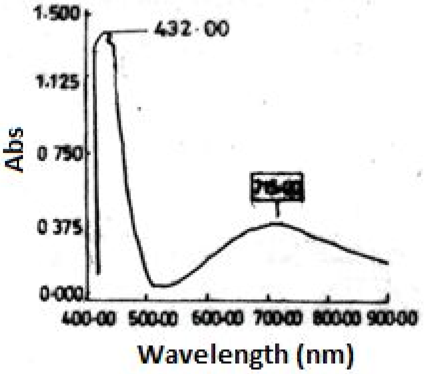

Fig 7. Visible spectra of [Cu(bipy)$_2$N$_3$(OClO$_3$)] (**1**)

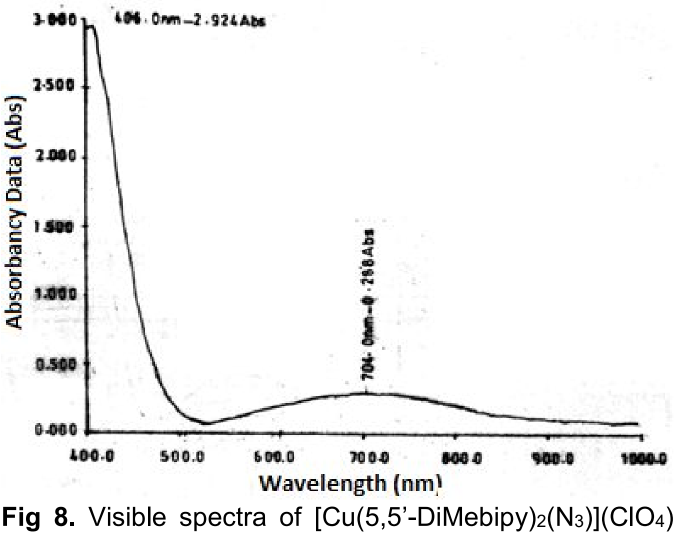

Fig 8. Visible spectra of [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) (**2**)

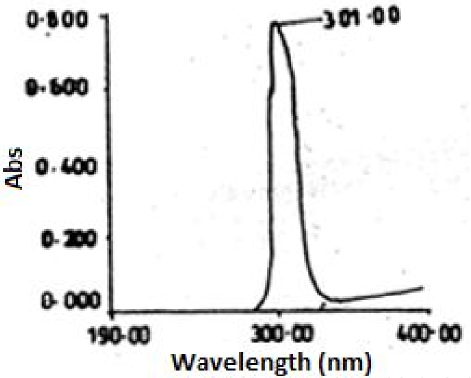

Fig 9. UV spectral of [Cu(bipy)$_2$N$_3$(OClO$_3$)] (**1**)

Table 8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for [Cu(bipy)$_2$ N$_3$(OClO$_3$)]

	x	y	z	U(eq)
H(1AA)	7788	9400	6322	26
H(2AA)	9073	10793	7048	33
H(3AA)	10344	9490	7089	34
H(4AA)	10297	6756	6431	28
H(7AA)	10132	4069	5908	31
H(8AA)	9833	1389	5182	35
H(9AA)	8423	620	4416	32
H(10B)	7341	2537	4412	26
H(1BA)	7659	4423	7073	26
H(2BA)	7215	2001	7638	32
H(3BA)	6012	421	6803	33
H(4BA)	5288	1327	5424	27
H(7BA)	4574	2659	4241	23
H(8BA)	4061	3695	2865	26
H(9BA)	4908	5597	2422	27
H(10A)	6232	6436	3365	25

mixing of angular momentum from excited states through spin –orbit coupling[41,58-59].

X-ray Structures

[Cu(bipy)$_2$N$_3$(OClO$_3$) (**1**): Complex (**1**) crystallized in the monoclinic space group P2$_1$/c, with the asymmetric unit (asu) comprising of Cu(**II**) centre, four nitrogen from two 2,2'-bipyridine ligands, one azide N$_3^-$ ligand and one oxygen from the perchlorate anion (Fig. 1). The coordination number of Cu(**II**) is six which defines a slightly distorted octahedral coordination geometry consisting of two bipyridyl units, a perchlorate group and an azide moiety. N(2A) and N(11) compose the apical positions and N(1A), N(1B), N(2B) and O(2) occupy the basal plane. The Tables 6, 7 and 8 respectively show the atomic coordinates, equivalent isotropic displacement parameters and hydrogen coordinates parameters of this complex.

[Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) (**2**): This complex also crystallized in the monoclinic space group P2$_1$/c.

Table 9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Cu	2250(1)	1307(1)	180(1)	25(1)
N(1)	3365(1)	2359(2)	815(1)	27(1)
N(2)	3159(1)	-398(2)	97(1)	26(1)
N(3)	1233(1)	177(2)	-529(1)	26(1)
N(4)	1804(1)	-374(2)	824(1)	26(1)
N(11)	1572(1)	3401(3)	113(1)	37(1)
N(12)	1296(1)	4195(3)	-405(1)	35(1)
N(13)	1004(2)	5002(4)	-889(2)	64(1)
C(1)	3402(2)	3816(3)	1138(1)	33(1)
C(2)	4197(2)	4567(3)	1534(1)	37(1)
C(3)	4188(2)	6206(4)	1891(2)	55(1)
C(4)	4975(2)	3741(4)	1583(1)	40(1)
C(5)	4948(2)	2216(3)	1260(1)	36(1)
C(6)	4126(1)	1537(3)	874(1)	27(1)
C(7)	4006(1)	-69(3)	510(1)	27(1)
C(8)	4680(2)	-1214(3)	579(1)	37(1)
C(9)	4476(2)	-2710(3)	225(1)	40(1)
C(10)	3614(2)	-3065(3)	-201(1)	31(1)
C(11)	3362(2)	-4677(3)	-590(1)	39(1)
C(12)	2984(2)	-1845(3)	-246(1)	30(1)
C(13)	962(1)	578(3)	-1196(1)	29(1)
C(14)	214(2)	-131(3)	-1684(1)	30(1)
C(15)	-48(2)	372(4)	-2425(1)	44(1)
C(16)	-263(1)	-1278(3)	-1448(1)	30(1)
C(17)	15(1)	-1703(3)	-761(1)	28(1)
C(18)	779(1)	-976(3)	-305(1)	24(1)
C(19)	1151(1)	-1391(3)	438(1)	25(1)
C(20)	863(2)	-2732(3)	728(1)	32(1)
C(21)	1240(2)	-3008(3)	1429(1)	36(1)
C(22)	1894(2)	-1932(3)	1838(1)	31(1)
C(23)	2304(2)	-2131(4)	2604(1)	42(1)
C(24)	2159(1)	-642(3)	1502(1)	29(1)
Cl(1)	2871(1)	3023(1)	2951(1)	37(1)
O(1)	3559(2)	1907(4)	2948(2)	65(1)
O(2)	2165(2)	2051(4)	3049(2)	65(1)
O(3)	3166(2)	4252(4)	3463(2)	69(1)
O(4)	2477(2)	3779(4)	2280(1)	70(1)
O(1A)	3500(8)	4401(15)	2927(9)	65(1)
O(2A)	2983(9)	3150(20)	3704(6)	65(1)
O(3A)	2066(8)	3200(20)	2547(8)	69(1)
O(4A)	3357(13)	1523(19)	2921(11)	70(1)

The crystal structure contains a Cu(**II**) centre, two molecules of 5,5'-DiMebipy-2,2'-bipyridine ligands and one azide N_3^- (Fig. 3) in the asu. The coordination geometry of the crystallographic center is close to square pyramidal with τ = 0.34, [τ = |β – α/60], where β and α represent the two largest angles around the central atom; τ =0 and 1 for the perfect pyramidal and trigonal bipyramidal geometries respectively [20]. The square base of the copper center is composed of the two 5,5'-DiMebipy-2,2'-bipyridine nitrogen atoms while the apical position is occupied by one azide nitrogen atom. The copper center in complex (**2**) is five coordinated and shows a distorted square pyramidal geometry as indicated by the τ value. The atomic coordinates of (**2**) is as shown in Table 9. The azide ions in the two complexes are nearly linear with 176.61(18)° and 176.7(3)° for N13-N12-N11 for [Cu(bipy)$_2$N$_3$(OClO$_3$) and [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) respectively which is similar to those reported [20]. In complex (1), adjacent units interact through strong C-H····O and N-H····N hydrogen bonding while in (**2**) only. Table 10 and Table 11 display the anisotropic displacement parameter and the hydrogen coordinates parameters of1 the complex. C-H····O hydrogen bonding exist, leading to the formation of infinite 3D supramolecular structures (Fig. 2 and Fig. 4). These supramolecular structures are close pack along the *a*-axis of the unit cell.

Table 10. Anisotropic displacement parameters (Å^{2}x 10^3) for [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U11	U22	U33	U23	U13	U12
Cu	20(1)	23(1)	31(1)	0(1)	7(1)	0(1)
N(1)	25(1)	27(1)	29(1)	-1(1)	10(1)	-3(1)
N(2)	21(1)	28(1)	28(1)	2(1)	8(1)	1(1)
N(3)	21(1)	25(1)	30(1)	2(1)	9(1)	4(1)
N(4)	21(1)	27(1)	30(1)	1(1)	9(1)	3(1)
N(11)	38(1)	32(1)	39(1)	-1(1)	9(1)	8(1)
N(12)	29(1)	29(1)	44(1)	-3(1)	11(1)	6(1)
N(13)	81(2)	56(2)	54(2)	17(1)	23(1)	35(2)
C(1)	33(1)	34(1)	35(1)	-3(1)	15(1)	-4(1)
C(2)	40(1)	42(1)	34(1)	-8(1)	17(1)	-13(1)
C(3)	52(2)	58(2)	60(2)	-29(2)	26(1)	-21(2)
C(4)	32(1)	50(2)	36(1)	-6(1)	10(1)	-15(1)
C(5)	24(1)	44(1)	36(1)	2(1)	8(1)	-5(1)
C(6)	24(1)	32(1)	26(1)	4(1)	8(1)	-2(1)
C(7)	22(1)	31(1)	27(1)	5(1)	8(1)	0(1)
C(8)	21(1)	44(1)	41(1)	0(1)	3(1)	6(1)
C(9)	32(1)	41(1)	45(2)	3(1)	11(1)	14(1)
C(10)	33(1)	30(1)	32(1)	3(1)	14(1)	6(1)
C(11)	44(1)	31(1)	44(1)	-1(1)	21(1)	7(1)
C(12)	24(1)	31(1)	33(1)	-2(1)	10(1)	2(1)
C(13)	27(1)	29(1)	31(1)	4(1)	12(1)	5(1)
C(14)	31(1)	30(1)	29(1)	-3(1)	9(1)	8(1)
C(15)	48(2)	50(2)	31(1)	-1(1)	8(1)	5(1)
C(16)	24(1)	32(1)	32(1)	-8(1)	6(1)	4(1)
C(17)	24(1)	24(1)	36(1)	-6(1)	12(1)	0(1)
C(18)	21(1)	22(1)	30(1)	-2(1)	11(1)	4(1)
C(19)	22(1)	23(1)	31(1)	-2(1)	11(1)	4(1)
C(20)	32(1)	26(1)	39(1)	0(1)	12(1)	-2(1)
C(21)	43(1)	27(1)	40(1)	7(1)	18(1)	2(1)
C(22)	34(1)	30(1)	32(1)	4(1)	13(1)	9(1)
C(23)	48(2)	41(2)	34(1)	9(1)	11(1)	8(1)
C(24)	26(1)	29(1)	30(1)	1(1)	7(1)	4(1)
Cl(1)	34(1)	29(1)	48(1)	6(1)	14(1)	5(1)
O(1)	38(1)	50(2)	110(2)	-2(2)	28(2)	15(1)
O(2)	53(2)	54(2)	101(2)	7(2)	42(2)	-2(1)
O(3)	53(2)	58(2)	70(2)	-26(2)	-11(1)	8(1)
O(4)	93(2)	65(2)	47(2)	18(1)	19(2)	22(2)
O(1A)	38(1)	50(2)	110(2)	-2(2)	28(2)	15(1)
O(2A)	53(2)	54(2)	101(2)	7(2)	42(2)	-2(1)
O(3A)	53(2)	58(2)	70(2)	-26(2)	-11(1)	8(1)
O(4A)	93(2)	65(2)	47(2)	18(1)	19(2)	22(2)

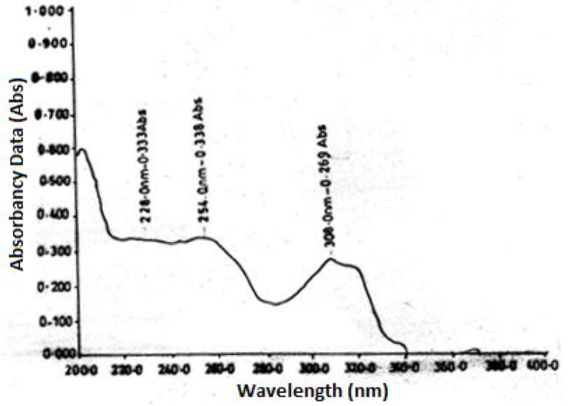

Fig 10. UV spectra of [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$)

CONCLUSION

Two mixed-ligand Cu(II) complexes [Cu(bipy)$_2$N$_3$(OClO$_3$)] (**1**) and [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) (**2**) have been synthesized and characterized by elemental analyses, infrared and electronic spectroscopies, room temperature magnetic susceptibility studies, molar conductance measurements and X-ray diffraction analyses. In this work, we have successfully synthesized two mixed ligand azido complexes with different substituents on the 2,2'-bipyridine rings, having a different geometrical arrangement of the groups around the central copper ion as elucidated by the X-ray analyses. This difference

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$)

	x	y	z	U(eq)
H(1AA)	2860	4366	1095	40
H(3AA)	4783	6707	2037	82
H(3AB)	4015	6011	2294	82
H(3AC)	3760	6967	1573	82
H(4AA)	5532	4226	1840	48
H(5AA)	5483	1640	1301	43
H(8AA)	5274	-974	866	45
H(9AA)	4933	-3509	274	48
H(11A)	2719	-4692	-840	58
H(11B)	3524	-5618	-266	58
H(11C)	3677	-4775	-917	58
H(12A)	2390	-2050	-540	35
H(13A)	1294	1381	-1344	34
H(15A)	-472	-444	-2712	66
H(15B)	482	406	-2558	66
H(15C)	-325	1482	-2488	66
H(16A)	-785	-1774	-1762	36
H(17A)	-314	-2487	-600	33
H(20A)	411	-3455	448	39
H(21A)	1052	-3935	1632	43
H(23A)	2443	-1026	2820	63
H(23B)	2852	-2790	2715	63
H(23C)	1885	-2708	2778	63
H(24A)	2617	88	1768	35

in geometry between these two complexes may be attributed to the steric effect of the methyl substituents on the [Cu(5,5'-DiMebipy)$_2$(N$_3$)](ClO$_4$) complex even though the reaction ratios and solvents used were different. The dielectric constant of water may likely be the reason for the interaction between the perchlorate anion and the solvent thereby leading to compound (**2**) with the perchlorate anion non -coordinating. The solvent in complex (**1**) provided a platform for the coordination of the perchlorate anion due to its less ability to interact with the perchlorate anion.

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