

Mixed-Ligand Complexes of Bis(4,4'-DiMeBipy-2,2'-bipyridine)copper(II) Perchlorate with Pseudohalide Ligands: Synthesis, Characterization and X-ray Structures

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Abstract: The synthesis, characterization and single crystal x-ray diffraction studies of [Cu(4,4'-DimeBipy)₂(N₃)₂](ClO₄)₂.CH₃CN (**1**), [Cu(4,4'-DimeBipy)₂(NCS)](SCN) (**2**) and [Cu(4,4'-DimeBipy)₂(Cl)]₂(ClO₄)₂.H₂O.CH₃CN (**3**) are reported. The complexes were characterized by employing elemental analyses (CHN), infrared and UV-Visible spectroscopy and single crystal x-ray diffraction. Compound (**1**) is monoclinic, with *a* = 10.8606(12) Å, *b* = 34.533(4) Å, *c* = 14.4465(16) Å, β = 103.495(2)°, *P* 21/*c* space group, with final *R*1 = 0.0497, *wR*2 = 0.1151, compound (**2**) also is monoclinic with *a* = 22.837(2) Å, *b* = 8.3902(7) Å, *c* = 13.7627(11) Å, β = 90.024(3)°, *P* 2/*c* space group, with final *R*1 = 0.0939, *wR*2 = 0.2627 while compound (**3**) is triclinic, with *a* = 11.1857(9), *b* = 14.2140(12) Å, *c* = 17.7116(14) Å, α = 106.698(4)°, β = 93.267(4)°, γ = 104.241(4)°, *P* -1 space group, with final *R*1 = 0.0602, *wR*2 = 0.1612. The elemental analyses in conjunction with the x-ray experiment gave the formula for compounds (**1**), (**2**) and (**3**). The CuN₅ chromospheres in (**1**) and (**2**) and CuN₄Cl in (**3**) each has the Cu atom to be five-coordinate in a square pyramidal geometry with four N atoms from the 2,2'-bipyridine derivative in the basal plane and N atom of the azide ligand (**1**), the N atom of the isothiocyanate ligand (**2**) and chloride ligand (**3**) occupying the apical positions.

Keyword: Azide ligand, *P*-1 Space group, Chromophores, Monoclinic, 4,4'-DimeBipy, Basal plane

Introduction

Complexes of polypyridyl ligands in recent times have attracted a lot of attention due to their potential application in photolysis, molecular electronic and material science, catalysis,

electrochemistry, biochemistry, ring-opening metathesis, molecular scaffolding for supramolecular assemblies *etc*¹⁻³. As a result of their versatile structures and wide applications, polynuclear complexes play an important role in coordination chemistry⁴. Polynuclear complexes are efficiently assembled by the use of suitable bridging ligands N_3^- , NCS^- , CN^- , Cl^- , NCO^- *etc*⁴⁻⁸. N_3^- , NCS^- , NCO^- are known to be extremely versatile ligands in the field of coordination chemistry and as ligands that can bridge, they can form a rich structural variety of polynuclear complexes which have interesting magnetic interactions by propagating the magnetic interaction between the paramagnetic centers of adjacent metal ions ranging between antiferromagnetic to ferromagnetic couplings⁸⁻¹⁰. Azide and thiocyanate are particularly interesting among the bridging ligands due to their different coordination modes which could be end-on, end-to-end and many other modes^{4,11,12}. In this paper, we report the synthesis and structural details of the three mixed-ligand complexes of $Cu(4,4'$ -DimeBipy)₂(ClO₄)₂ with azide, isothiocyanate and chlorine as ligands, $[Cu(4,4'$ -DimeBipy)₂(N₃)₂](ClO₄)₂·CH₃CN (**1**), $[Cu(4,4'$ -DimeBipy)₂(NCS)]SCN (**2**) and $[Cu(4,4'$ -DimeBipy)₂(Cl)]₂(ClO₄)₂·H₂O·CH₃CN (**3**). The effects of the different pseudohalide ligands investigated.

Experimental

4,4'-Dimethyl-2,2'-bipyridine, copper perchlorate hexahydrate, sodium azide, sodium thiocyanate, potassium chloride and other reagents were purchased from Aldrich Chemical Co., Burgoyne Burbidges and Co., India and were used without further purification. Bis-(4,4'-dimethyl-2,2'-bipyridine)copper perchlorate, $Cu(4,4'$ -dimeBipy)₂(ClO₄)₂ was synthesized according to literature¹³.

Physical measurements

CHN analyses were carried out by Atlantic Microlab, Atlanta GA. Electronic spectra were recorded on a Genesys 10 UV-Visible spectrophotometer. Infrared spectra were recorded on a Perkin - Elmer PE 100 spectrometer with an attenuated total reflectance (ATR) window.

Caution

Perchlorates are potentially explosive. So also are azido compounds especially in the presence of organic ligands¹⁴. Only a small amount of these materials should be prepared and handled with care.

X-ray diffraction analysis

Single crystals of the $[Cu(4,4'$ -DimeBipy)₂(N₃)₂](ClO₄)₂·CH₃CN(**1**), $[Cu(4,4'$ -DimeBipy)₂(NCS)]SCN (**2**) and $[Cu(4,4'$ -DimeBipy)₂(Cl)]₂(ClO₄)₂·H₂O·CH₃CN (**3**) complexes for x-ray diffraction experiments were obtained by slow evaporation of the acetonitrile solution of the compounds. Cell parameters and data were collected using a Bruker Apex 2 CCD diffractometer using standard programs.

Synthesis of $[Cu(4,4'$ -DimeBipy)₂(N₃)₂](ClO₄)₂·CH₃CN(**1**)

$[Cu(4,4'$ -DimeBipy)₂](ClO₄)₂ (0.20 mmol, 0.126 g) and 1.8 mmol (0.12 g) sodium azide in distilled water (30 mL) was refluxed for 3 h. The highly crystalline green compound obtained was filtered by suction, washed with distilled water and dried in the air. Green single crystals suitable for x-ray diffraction experiment were obtained from acetonitrile solution of the compound. Anal. Calcd for C₅₀H₅₁N₁₅O₈Cl₂Cu₂ (%) C, 49.59; H, 4.33; N, 16.69. Found: C, 49.28; H, 4.21; N, 16.80. Yield: 0.0947 g, (83%). ATRIR ν/cm^{-1} : 1028vs, 843 m (ClO₄), 2059 s (N₃). UV-Vis (CH₃CN) λ_{max}/cm^{-1} : 14025 (713 nm), 33898 (295 nm), 48077 (208 nm).

Synthesis of [Cu(4,4'-DimeBipy)₂(NCS)]SCN(2)

0.231 g (2.85 mmole) Sodium thiocyanate was added to a solution of 0.200 g (0.32 mmole) Cu(4,4'-DiMeBipy)₂(ClO₄)₂ dissolved in 30 mL distilled water in a 100 mL round bottom flask and the mixture refluxed for 2 h. The lemon-green 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 by slow evaporation of acetonitrile solution of the compound. Anal. Calcd for C₂₆H₂₆N₆S₂OCu(%) C 55.14, H 4.63, N 14.85 %; found: C 56.74, H 4.41, N 15.39 %. Yield: 0.104g, (60%). ATRIR ν/cm^{-1} : $\nu(\text{C-N})$: 2090vs, 2054vs; $\nu(\text{C-S})$: 828vs, 733 $\text{m}^{10,15}$. UV-Vis (CH₃CN) $\lambda_{\text{max}}/\text{cm}^{-1}$: 10605 (943 nm), 14535 (688 nm), 25510 (392 nm), 32680sh (306 nm), 34247 (292 nm), 43668 (229 nm), 49261 (203 nm).

Synthesis of [Cu(4,4'-DimeBipy)₂(Cl)]₂(ClO₄)₂H₂O.CH₃CN(3)

Potassium chloride (1.8 mmol, 0.134 g) and [Cu(4,4'-DimeBipy)₂](ClO₄)₂ (0.2 mmole, 0.1262 g) dissolved in 30 mL distilled water and the mixture was stirred and heated to reflux for 3 h. The turquoise blue solution obtained was cooled to room temperature before filtration by suction and washed with distilled water. The compound was then dried in the air. Single crystals suitable for x-ray diffraction analysis were obtained by slow evaporation of the solution of the compound in CH₃CN. Anal. Calcd for C₅₀H₅₃N₉O₉Cl₄Cu₂ (%) C, 48.50; H, 4.58; N, 9.44. Found: C, 48.20; H, 4.61; N, 8.53; Yield: 0.0682 g (98 %). ATRIR ν/cm^{-1} : 1069vs, 820 $\text{m}(\text{ClO}_4)^{16}$. UV-Vis (CH₃CN) $\lambda_{\text{max}}/\text{cm}^{-1}$: 13568 (738 nm) br, 33841 (296 nm), 48077 (208 nm).

Results and Discussion

Three mixed-ligand Cu(II) complexes of 4,4'-dimethyl-2,2'-bipyridine complexes with azide (N₃⁻), isothiocyanate (NCS⁻) and Cl⁻ were isolated with the azide and chloride complexes being dimeric while the isothiocyanate complex is a pseudo-merohedral twin which crystallized in the monoclinic system but the beta angle was close to 90°, Table 1. Their solid-state structures elucidated by x-ray diffraction analysis gave the molecular formula [Cu(4,4'-DimeBipy)₂(N₃)₂](ClO₄)₂.CH₃CN(1), [Cu(4,4'-DimeBipy)₂(NCS)]SCN(2) and [Cu(4,4'-DimeBipy)₂(Cl)]₂(ClO₄)₂H₂O.CH₃CN (3). The infrared spectra of complex (1) display a strong band at 2059 cm^{-1} which is attributed to $\nu_{\text{asym}}(\text{N}_3)$ absorption band^{6,17}. In the complex (2), the $\nu(\text{C-N})$ of the NCS¹⁸ was at 2090 cm^{-1} and 2054 cm^{-1} , while the $\nu(\text{C-S})$ ^{18,19} was at 828 cm^{-1} and 733 cm^{-1} . The coordinated thiocyanate group is quasi-linear with the values 176.7°{N(1S) – C(1S) – S(1S)} and 171.3°{N(2S) – C(2S) – S(2S)} respectively for the two pseudo-merohedral twin while the uncoordinated group is observed to be linear Table 4, the bent coordination of thiocyanate ligand is much more scarce when compared with the linear one. This structural feature is in agreement with that observed in structurally characterized complexes containing N-bound thiocyanato group¹⁰. The bands centered at 2059 cm^{-1} and 2090 cm^{-1} and 2054 cm^{-1} respectively for both the azide and isothiocyanate complexes characterize the coordination of the two pseudohalides to the copper center. However, for complex (3) with chlorine as the ligand, there is no band observed at this wave number region in agreement to reported structurally similar system¹⁹. Both complexes (1) and (3) display the broad and intense band between 1016-1069 cm^{-1} and another band at approximately 762-829 cm^{-1} both are consistent with the characteristic peak of ClO₄⁻ anion^{6,16}.

Table 1. Crystallographic and refinement data for complexes [Cu(4,4'-DimeBipy)₂(N₃)₂(ClO₄)₂.CH₃CN (**1**), [Cu(4,4'-DimeBipy)₂(NCS)](SCN) (**2**) and [Cu(4,4'-DimeBipy)₂(Cl)]₂(ClO₄)₂H₂O.CH₃CN (**3**)

	1	2	3
Empirical formula	C ₅₀ H _{51.50} Cl ₂ Cu ₂ N ₁₅ O _{8.25}	C ₂₆ H ₂₆ S ₂ Cu N ₆ O	C ₅₀ H ₅₃ Cl ₄ Cu ₂ N ₉ O ₉
Formula weight	1193.45	566.19	1192.89
Temperature	100(2)K	100(2)K	100(2)K
Wavelength	0.71073 Å	0.71073 Å	1.54178 Å
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P 21/c	P 2/c	P- 1
Unit cell dimensions	a = 10.8606(12) Å b = 34.533(4) Å c = 14.4465(16) Å α = 90° β = 103.495(2)° γ = 90°	a = 22.837(2) Å b = 8.3902(7) Å c = 13.7627(11) Å α = 90° β = 90.024(3)° γ = 90°	a = 11.1857(9) Å b = 14.2140(12) Å c = 17.7116(14) Å α = 106.698(4)° β = 93.267(4)° γ = 104.241(4)°
Volume	5268.6(10) Å ³	2637.1(4) Å ³	2589.6(4) Å ³
Z	4	4	2
Density (calculated)	1.505 Mg/m ³	1.426 Mg/m ³	1.530 Mg/m ³
Absorption coefficient	0.978 mm ⁻¹	1.018 mm ⁻¹	3.454 mm ⁻¹
F(000)	2460	1172	1228
θ range for data collection, deg	1.179 -28.386	2.317-30.574	2.629-67.919
Reflections collected	48650	32806	72178
Independent reflections	13155 [R(int) = 0.0295]	7940 [R(int) = 0.0564]	72178 [R(int) = n/a]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.5885	0.7461 and 0.5693	0.7529 and 0.3990
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	13155/69/769	7940/36/336	72178/18/708
Goodness-of-fit on F ²	1.073	1.062	1.064
Final R indices [I>2σ(I)]	R1 = 0.0497, wR2 = 0.1151	R1 = 0.0939, wR2 = 0.2627	R1 = 0.0602, wR2 = 0.1612
R indices (all data)	R1 = 0.0595, wR2 = 0.1196	R1 = 0.1136, wR2 = 0.2794	R1 = 0.0652, wR2 = 0.1659
Extinction coefficient	n/a	0.0040(9)	n/a

The electronic transitions of a square pyramidal copper in a five-coordinate ligand field has the one-electron ground state configuration to be $d_{x^2-y^2}^2 > d_{z^2} > d_{xy} > d_{xz} \approx d_{yz}$. The complexes with the value of $\tau = 0.23, 0.0004$ and 0.22 respectively²⁰ show the d-d transition with high-intensity peak at $14\,025\text{ cm}^{-1}$ for (1), $14\,535\text{ cm}^{-1}$ (2) and $13\,568\text{ cm}^{-1}$ for (3), only complex (2) shows the low-energy, low-intensity shoulder at $10\,605\text{ cm}^{-1}$ (943 nm). These high-intensity absorption bands⁶ are attributed to the $d_{xz} \approx d_{yz} \rightarrow d_{x^2-y^2}$ which is also a confirmation of the square pyramidal geometries for the Cu(II) center in the complexes as observed in the crystal structures while the low-energy, low-intensity band in (2) is assigned to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition which is in accordance to similar systems⁶. Also in complex (2), in addition to the d-d transition, an intense band at $25\,510\text{ cm}^{-1}$ (392 nm) with a shoulder at $32\,680\text{ cm}^{-1}$ (306 nm) indicating a ligand-to-metal charge transfer ($\pi \rightarrow d_o$) transition was observed²¹. In the three complexes, in addition to the d-d transitions, bands below 300 nm observed at $33\,898\text{ cm}^{-1}$ (295 nm), $48\,077\text{ cm}^{-1}$ (208 nm) for (1), $34\,247\text{ cm}^{-1}$ (292 nm), $43\,668\text{ cm}^{-1}$ (229 nm), $49\,261\text{ cm}^{-1}$ (203 nm) (2) and $33\,841\text{ cm}^{-1}$ (298 nm), $48\,077\text{ cm}^{-1}$ (208 nm) (3) can be assigned to the $\pi \rightarrow \pi^*$ transitions of the pyridine rings^{1,2,21}.

Crystal structures

The structural analyses reveal that two of the three complexes are isostructural and are dimeric (Figure 2 and Figure 6). The ORTEP diagrams with atom numbering schemes of (1), (2) and (3) are shown in Figures 1, 3 and 5 respectively.

[Cu(4,4'-DimeBipy)₂(N₃)₂(ClO₄)₂·CH₃CN (1): Complex (1) crystallized in the monoclinic centrosymmetrical P 2₁/c space group (Table 1) with the Cu center surrounded by four N atoms of 4,4'-dimethyl-2,2'-bipyridine and one N atom of an azide ligand in the apical position (Figure 1).

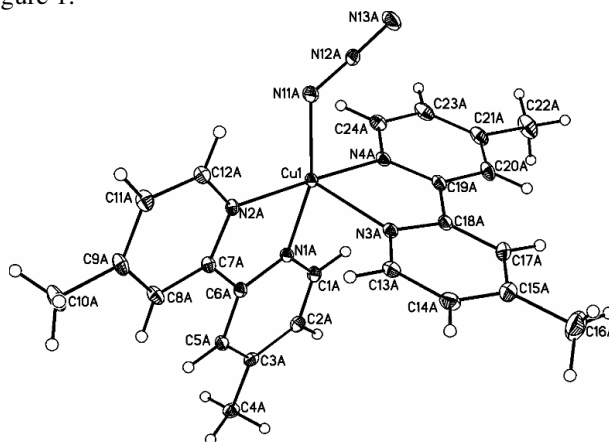


Figure 1. ORTEP representation of the solid-state molecular structure for [Cu(4,4'-DimeBipy)₂(N₃)₂(ClO₄)₂·CH₃CN (1)

The basal plane is defined by the Cu(1A) – N(1A) $2.0383(17)\text{ \AA}$, Cu(1A) – N(2A) $2.0033(16)\text{ \AA}$, Cu(1A) – N(3A) $2.1828(18)\text{ \AA}$ and Cu(1A) – N(4A) $2.0111(16)\text{ \AA}$ as in Table 2 with the bond lengths longer than that of the unsubstituted starting complex, Cu(bipy)₂(ClO₄)₂ with Cu(1) – N(1) $1.988(4)\text{ \AA}$, Cu(1) – N(2) $1.996(4)\text{ \AA}$, Cu(1) – N(3) $1.984(4)\text{ \AA}$ and Cu(1) – N(4) $2.005(4)\text{ \AA}$ ²². The increase in bond lengths may be attributed to the presence of the azide ligand in (1). The apical position occupied by the azide ligand has the bond length for the Cu(1A)–N(11A) to be $1.9679(19)\text{ \AA}$.

Table 2. Bond lengths [\AA] and angles [$^\circ$] for $[\text{Cu}(4,4'\text{-DimeBipy})_2(\text{N}_3)_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$

Cu(1)-N(11A)	1.9679(19)
Cu(1)-N(2A)	2.0033(16)
Cu(1)-N(4A)	2.0111(16)
Cu(1)-N(1A)	2.0383(17)
Cu(1)-N(3A)	2.1828(18)
N(11A)-Cu(1)-N(2A)	91.34(7)
N(11A)-Cu(1)-N(4A)	92.72(7)
N(2A)-Cu(1)-N(4A)	175.04(7)
N(11A)-Cu(1)-N(1A)	162.46(8)
N(2A)-Cu(1)-N(1A)	80.37(7)
N(4A)-Cu(1)-N(1A)	94.95(7)
N(11A)-Cu(1)-N(3A)	103.34(8)
N(2A)-Cu(1)-N(3A)	103.17(7)
N(4A)-Cu(1)-N(3A)	78.66(7)
N(1A)-Cu(1)-N(3A)	93.64(7)
N(13A)-N(12A)-N(11A)	177.9(2)
O(14)-Cl(1)-O(11)	109.82(14)
O(14)-Cl(1)-O(13)	108.92(14)
O(11)-Cl(1)-O(13)	109.50(14)
O(14)-Cl(1)-O(12)	110.53(15)
O(11)-Cl(1)-O(12)	109.58(11)
O(13)-Cl(1)-O(12)	108.45(12)
O(24)-Cl(2)-O(22)	109.56(17)
O(24)-Cl(2)-O(21)	108.89(14)
O(22)-Cl(2)-O(21)	110.05(13)
O(24)-Cl(2)-O(23)	108.94(14)
O(22)-Cl(2)-O(23)	108.21(14)
O(21)-Cl(2)-O(23)	111.17(13)
H(1W1)-O(1W)-H(1W2)	103(3)

The bite angles in (**1**) reduced considerably compared to that of the starting unsubstituted complex except in $\text{N}(2\text{A}) - \text{Cu} - \text{N}(4\text{A})$ $175.04(7)$ and $\text{N}(2\text{A}) - \text{Cu} - \text{N}(3\text{A})$ $103.17(7)$ for (**1**) as compared to $\text{N}(2) - \text{Cu} - \text{N}(4)$ $151.8(2)$ and $\text{N}(2) - \text{Cu} - \text{N}(3)$ $102.0(2)^{22}$. This may be because the ClO_4^- anion is significantly larger than the N_3^- anion. The azide ligand is nearly linear $\text{N}(13\text{A})-\text{N}(12\text{A})-\text{N}(11\text{A})$ $177.9(2)^\circ$ in its coordination to the copper atom⁴. Two intramolecular hydrogen bonding exist in (**1**), $\text{C}-\text{H} \cdots \text{N}$ which involves the N atom of the unbound CH_3CN molecule and the hydrogen atom of the bipyridine ring and also the $\text{Cl}-\text{O} \cdots \text{H}$ between the ClO_4^- and the hydrogen atom of the bipyridine ring. The intermolecular hydrogen bonds, $\text{C}-\text{H} \cdots \text{N}$ that exist between the adjacent units of (**1**) Figure 2 involves N atom of the N_3^- ligand and one of the hydrogen atom of the methyl group on the ring. The hydrogen bond parameters are displayed in Table 3.

These hydrogen bonds contribute to the packing stability. A closer packing is also achieved by the overlapping of the substituted bipyridine ligands of twoneighboring molecules within a sheet. $[\text{Cu}(4,4'\text{-DimeBipy})_2(\text{NCS})][\text{SCN}]$: (**2**) crystallized in the monoclinic $\text{P}2_1/\text{c}$ space group with coordination polyhedron around the copper center best described as a distorted square pyramidal as exemplified by its tau parameter ($\tau = 0.0004$)²⁰ with CuN_5 chromophore (Figure 3).

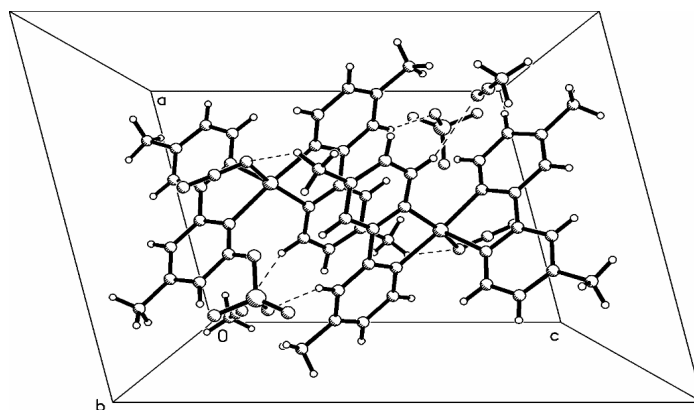


Figure 2. b-axis projection of the crystal structure $[\text{Cu}(4,4'\text{-DimeBipy})_2(\text{N}_3)]_2(\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$

Table 3. Hydrogen bonds for $[\text{Cu}(4,4'\text{-DimeBipy})_2(\text{N}_3)]_2(\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ [\AA and $^\circ$]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1A)-H(1AA)...N(4A)	0.95	2.65	3.170(3)	115.0
C(1A)-H(1AA)...N(1S)	0.95	2.68	3.488(4)	142.6
C(2A)-H(2AA)...O(14)	0.95	2.58	3.428(3)	148.1
C(8A)-H(8AA)...O(24)	0.95	2.41	3.303(3)	156.5
C(12A)-H(12A)...N(11A)	0.95	2.45	2.982(3)	115.3
C(12A)-H(12A)...O(1W)#1	0.95	2.53	3.250(9)	132.4
C(14A)-H(14A)...O(12)#2	0.95	2.55	3.238(3)	129.7
C(17A)-H(17A)...N(13A)#3	0.95	2.37	3.297(3)	165.5
C(20A)-H(20A)...N(13A)#3	0.95	2.69	3.628(3)	169.1
C(24A)-H(24A)...O(24)#1	0.95	2.63	3.366(3)	134.4
C(1B)-H(1BA)...O(13)	0.95	2.39	3.229(3)	147.2
C(2B)-H(2BA)...O(1W)	0.95	2.46	3.217(9)	136.2
C(5B)-H(5BA)...N13Ba#4	0.95	2.68	3.607(5)	163.8
C(5B)-H(5BA)...N13Cb#4	0.95	2.57	3.416(13)	149.2
C(11B)-H(11B)...O(13)#5	0.95	2.64	3.498(3)	150.1
C(12B)-H(12B)...N11Dc	0.95	2.42	2.976(10)	117.2
C(17B)-H(17B)...N11Cb#6	0.95	2.66	3.545(10)	155.9
C(20B)-H(20B)...N11Ba#6	0.95	2.54	3.359(5)	144.5
C(20B)-H(20B)...N11Cb#6	0.95	2.59	3.417(10)	146.3
C(24B)-H(24B)...O(22)	0.95	2.56	3.270(3)	132.2
O(1W)-H(1W1)...O(24)#7	0.826(19)	2.31(2)	3.127(9)	168(7)
O(1W)-H(1W2)...O(11)	0.828(19)	2.15(3)	2.789(9)	134(4)
C(2S)-H(2S1)...N11Ba#6	0.98	2.55	3.516(6)	169.6
C(2S)-H(2S1)...N11Cb#6	0.98	2.47	3.426(11)	166.2
C(2S)-H(2S1)...N11Cb#6	0.98	2.50	3.449(10)	162.4
C(2S)-H(2S1)...N13Dc#6	0.98	2.12	2.903(19)	135.4
C(2S)-H(2S3)...O(12)	0.98	2.53	3.480(5)	163.0

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$ #2 $x+1, y, z$ #3 $-x+1, -y+1, -z$ #4 $x, -y+1/2, z+1/2$ #5 $x+1, -y+1/2, z+1/2$ #6 $x, -y+1/2, z-1/2$, #7 $x-1, y, z$

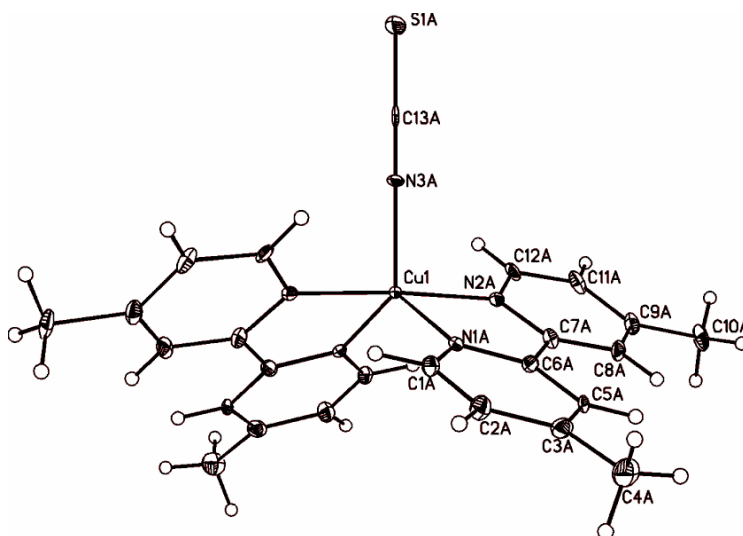


Figure 3. ORTEP representation of the solid-state molecular structure for $[\text{Cu}(4,4'\text{-DimeBipy})_2(\text{NCS})]\text{SCN}$

The complex (**2**) as revealed by the x-ray diffraction studies is a merohedral twin which crystallized in the monoclinic system but the beta angle was close to 90° (90.024°) so it emulate an orthorhombic system. The isothiocyanate group that coordinated is quasi-linear and the bond lengths $\text{Cu}(1) - \text{N}(1\text{A})$ 2.083(5) Å, $\text{Cu}(1) - \text{N}(1\text{A})\#1$ 2.083(5) Å, $\text{Cu}(1) - \text{N}(2\text{A})$ 1.999(5) Å and $\text{Cu}(1) - \text{N}(2\text{A})\#1$ 1.999(5) and $\text{Cu}(1) - \text{N}(3\text{A})$ 1.979(6) are obtained as observed in Table 4.

Table 4. Bond lengths [Å] and angles [$^\circ$] for $[\text{Cu}(4,4'\text{-DimeBipy})_2(\text{NCS})]\text{SCN}$

$\text{Cu}(1)\text{-N}(3\text{A})$	1.979(6)
$\text{Cu}(1)\text{-N}(2\text{A})\#1$	1.999(5)
$\text{Cu}(1)\text{-N}(2\text{A})$	1.999(5)
$\text{Cu}(1)\text{-N}(1\text{A})\#1$	2.083(5)
$\text{Cu}(1)\text{-N}(1\text{A})$	2.083(5)
$\text{S}(1\text{A})\text{-C}(13\text{A})$	1.627(9)
$\text{N}(1\text{A})\text{-C}(1\text{A})$	1.352(8)
$\text{N}(1\text{A})\text{-C}(6\text{A})$	1.356(7)
$\text{N}(2\text{A})\text{-C}(12\text{A})$	1.335(8)
$\text{N}(2\text{A})\text{-C}(7\text{A})$	1.359(8)
$\text{N}(3\text{A})\text{-C}(13\text{A})$	1.149(11)
$\text{Cu}(2)\text{-N}(1\text{B})\#2$	1.974(7)
$\text{Cu}(2)\text{-N}(1\text{B})$	1.974(7)
$\text{Cu}(2)\text{-N}(3\text{B})$	2.039(14)
$\text{Cu}(2)\text{-N}(2\text{B})\#2$	2.082(8)
$\text{Cu}(2)\text{-N}(2\text{B})$	2.082(8)
$\text{S}(1\text{B})\text{-C}(13\text{B})$	1.602(9)
$\text{N}(1\text{B})\text{-C}(6\text{B})$	1.343(9)
$\text{N}(1\text{B})\text{-C}(1\text{B})$	1.356(12)

Contd...

N(2B)-C(12B)	1.316(12)
N(2B)-C(7B)	1.332(9)
N(3B)-C(13B)	1.121(16)
S(1S)-C(1S)	1.608(12)
C(1S)-N(1S)	1.145(14)
S(2S)-C(2S)	1.581(14)
C(2S)-N(2S)	1.130(16)
O(1W)-H(1W2)	0.85(2)
O(1W)-H(1W1)	0.84(2)
N(3A)-Cu(1)-N(2A)#1	92.03(13)
N(3A)-Cu(1)-N(2A)	92.03(13)
N(2A)#1-Cu(1)-N(2A)	175.9(3)
N(3A)-Cu(1)-N(1A)#1	117.82(13)
N(2A)#1-Cu(1)-N(1A)#1	80.41(19)
N(2A)-Cu(1)-N(1A)#1	97.67(19)
N(3A)-Cu(1)-N(1A)	117.82(13)
N(2A)#1-Cu(1)-N(1A)	97.67(19)
N(2A)-Cu(1)-N(1A)	80.41(19)
N(1A)#1-Cu(1)-N(1A)	124.4(3)
N(3A)-C(13A)-S(1A)	180.0
N(1B)#2-Cu(2)-N(1B)	174.7(4)
N(1B)#2-Cu(2)-N(3B)	92.7(2)
N(1B)-Cu(2)-N(3B)	92.7(2)
N(1B)#2-Cu(2)-N(2B)#2	79.6(3)
N(1B)-Cu(2)-N(2B)#2	97.8(3)
N(3B)-Cu(2)-N(2B)#2	118.5(2)
N(1B)#2-Cu(2)-N(2B)	97.8(3)
N(1B)-Cu(2)-N(2B)	79.6(3)
N(3B)-Cu(2)-N(2B)	118.5(2)
N(2B)#2-Cu(2)-N(2B)	123.1(4)
N(3B)-C(13B)-S(1B)	180.0
N(1S)-C(1S)-S(1S)	175.5(14)
N(2S)-C(2S)-S(2S)	171.7(16)
H(1W2)-O(1W)-H(1W1)	99(3)

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

A slight variation is observed between the bond lengths of (**2**) compared to those of Cu(bipy)₂(ClO₄)₂. Hydrogen bonding (Table 5) exist between the oxygen atom of water molecule present in the crystal lattice and the hydrogen atom of the bipyridine ring; H-O---H and the nitrogen atom of the unbounded thiocyanate group with the hydrogen atom of the second water molecule present; C-N ---H Figure 4.

Table 5. Hydrogen bonds for [Cu(4,4'-DimeBipy)₂(NCS)](SCN) [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1A)-H(1AA)...S(1S)#3	0.95	2.91	3.615(8)	132.1
C(2A)-H(2AA)...O(1W)	0.95	2.61	3.445(15)	147.2
C(5A)-H(5AA)...S(1A)#4	0.95	2.93	3.873(6)	171.0
C(11A)-H(11A)...S(2S)#5	0.95	2.80	3.509(11)	132.2

Contd...

C(2B)-H(2BA)...S(2S)#6	0.95	2.83	3.512(13)	129.9
C(5B)-H(5BA)...S(1B)#7	0.95	2.99	3.940(9)	174.0
C(8B)-H(8BA)...S(1B)#7	0.95	2.94	3.883(9)	171.5
C(11B)-H(11B)...O(1W)	0.95	2.51	3.303(14)	140.8
C(12B)-H(12B)...S(1S)#3	0.95	2.86	3.560(12)	131.0
O(1W)-H(1W2)...S(1S)#3	0.85(2)	2.62(7)	3.216(12)	127(7)
O(1W)-H(1W2)...N(2S)#3	0.85(2)	2.37(6)	3.042(16)	136(7)
O(1W)-H(1W1)...N(1S)	0.84(2)	2.39(8)	2.992(14)	129(8)
O(1W)-H(1W1)...S(2S)	0.84(2)	2.58(7)	3.193(12)	131(8)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, -z+3/2$ #2 $-x+2, y, -z+3/2$ #3 $x, y+1, z$, #4 $-x+1, -y+2, -z+1$ #5 $-x+1, y+1, -z+3/2$ #6 $-x+2, y+1, -z+3/2$ #7 $-x+2, -y+2, -z+1$

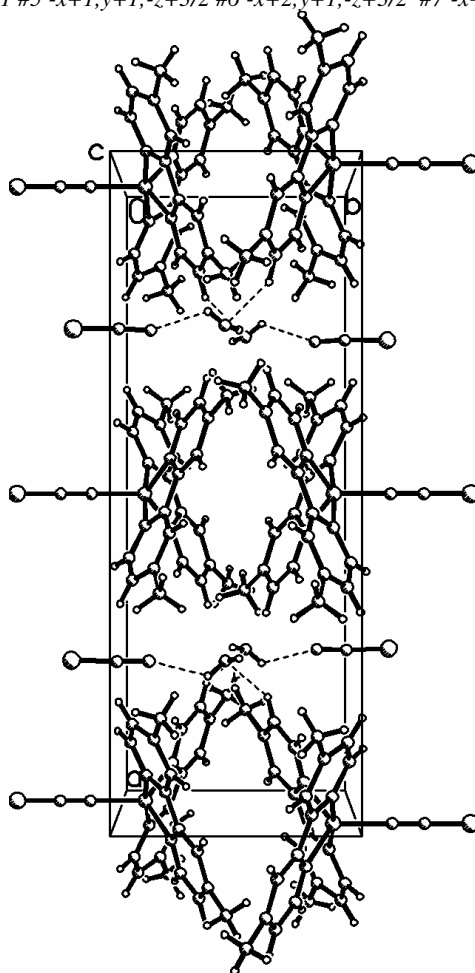


Figure 4. a-axis projection of the crystal structure $[\text{Cu}(4,4'\text{-DimeBipy})_2(\text{NCS})]\text{SCN}$

$[\text{Cu}(4,4'\text{-DimeBipy})_2(\text{Cl})]_2(\text{ClO}_4)_2\text{H}_2\text{O}\cdot\text{CH}_3\text{CN}$: The complex (**3**) crystallized in the triclinic $P\bar{1}$ space group with the basal plane constituted by four N atoms from two bidendate 4,4'-dimethyl -2,2'-bipyridine and one Cl atom of the chloride ligand occupying the apical position Figure 5.

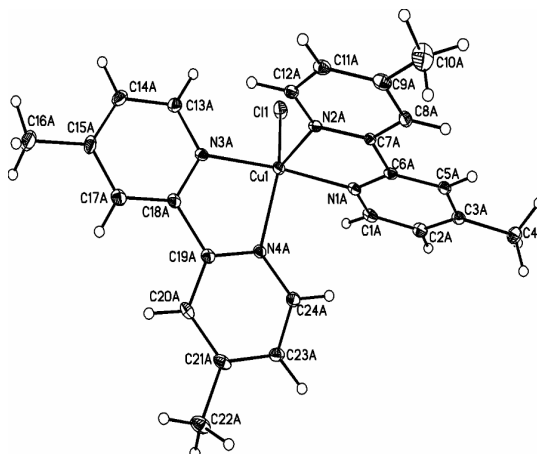


Figure 5. ORTEP representation of the solid-state molecular structure for $\text{Cu}(4,4'\text{-Dime Bipy})_2(\text{Cl})_2(\text{ClO}_4)_2\text{H}_2\text{O}.\text{CH}_3\text{CN}$

Increase in bond lengths were also observed in (**3**) $\text{Cu}(1\text{A}) - \text{N}(1\text{A})$ 2.002(3) Å, $\text{Cu}(1\text{A}) - \text{N}(2\text{A})$ 2.160(3) Å, $\text{Cu}(1\text{A}) - \text{N}(3\text{A})$ 2.002 (3) Å and $\text{Cu}(1\text{A}) - \text{N}(4\text{A})$ 2.068 (3) Å as in Table 6 relative to the $\text{Cu}(\text{bipy})_2(\text{ClO}_4)_2$ with $\text{Cu}(1) - \text{N}(1)$ 1.988(4) Å, $\text{Cu}(1) - \text{N}(2)$ 1.996(4) Å, $\text{Cu}(1) - \text{N}(3)$ 1.984 (4) Å and $\text{Cu}(1) - \text{N}(4)$ 2.005 (4) Å¹⁷.

Table 6. Bond lengths [Å] and angles [°] for $[\text{Cu}(4,4'\text{-DimeBipy})_2(\text{Cl})_2(\text{ClO}_4)_2\text{H}_2\text{O}.\text{CH}_3\text{CN}]$

$\text{Cu}(1)\text{-N}(1\text{A})$	2.002(3)
$\text{Cu}(1)\text{-N}(3\text{A})$	2.002(3)
$\text{Cu}(1)\text{-N}(4\text{A})$	2.068(3)
$\text{Cu}(1)\text{-N}(2\text{A})$	2.160(3)
$\text{Cu}(1)\text{-Cl}(1)$	2.2582(11)
$\text{N}(1\text{A})\text{-Cu}(1)\text{-N}(3\text{A})$	173.38(13)
$\text{N}(1\text{A})\text{-Cu}(1)\text{-N}(4\text{A})$	93.67(13)
$\text{N}(3\text{A})\text{-Cu}(1)\text{-N}(4\text{A})$	80.14(13)
$\text{N}(1\text{A})\text{-Cu}(1)\text{-N}(2\text{A})$	79.16(13)
$\text{N}(3\text{A})\text{-Cu}(1)\text{-N}(2\text{A})$	99.25(13)
$\text{N}(4\text{A})\text{-Cu}(1)\text{-N}(2\text{A})$	97.75(12)
$\text{N}(1\text{A})\text{-Cu}(1)\text{-Cl}(1)$	91.30(10)
$\text{N}(3\text{A})\text{-Cu}(1)\text{-Cl}(1)$	95.22(10)
$\text{N}(4\text{A})\text{-Cu}(1)\text{-Cl}(1)$	149.37(10)
$\text{N}(2\text{A})\text{-Cu}(1)\text{-Cl}(1)$	112.87(9)
$\text{N}(1\text{B})\text{-Cu}(2)\text{-N}(3\text{B})$	174.04(13)
$\text{N}(1\text{B})\text{-Cu}(2)\text{-N}(4\text{B})$	96.78(13)
$\text{N}(3\text{B})\text{-Cu}(2)\text{-N}(4\text{B})$	80.30(13)
$\text{N}(1\text{B})\text{-Cu}(2)\text{-N}(2\text{B})$	80.03(13)
$\text{N}(3\text{B})\text{-Cu}(2)\text{-N}(2\text{B})$	95.35(13)
$\text{N}(4\text{B})\text{-Cu}(2)\text{-N}(2\text{B})$	100.74(12)
$\text{N}(1\text{B})\text{-Cu}(2)\text{-Cl}(2)$	92.44(10)
$\text{N}(3\text{B})\text{-Cu}(2)\text{-Cl}(2)$	93.36(10)
$\text{N}(4\text{B})\text{-Cu}(2)\text{-Cl}(2)$	132.31(9)
$\text{N}(2\text{B})\text{-Cu}(2)\text{-Cl}(2)$	126.94(10)

The Cu(1)-Cl(1) 2.2582(11) bond length is longer than the Cu(1A)-N(11A) 1.9679 (19) of (3) this slight difference may be attributed to the size and the electronegativity of the Cl⁻ anion. The bite angles in (3) also reduced considerably in comparison to the unsubstituted complex except in N(1A) – Cu – N(3A) 173.38 (13) Table 6 for (3) as compared to N(1) – Cu – N(3) 161.8 (2)²². The coordination geometry of the crystallographic center is close to square pyramidal with $\tau = 0.22$, $[\tau = |\beta - \alpha/60|]$, where β and α represent the two largest angles around the central atom; $\tau = 0$ and 1 for the perfect pyramidal and trigonalbipyramidal geometries respectively¹⁹. There are four forms of hydrogen bonding in complex (3). C(14A)-H(14A)...O1WAa#2, C(14A)-H(14A)...O1WBb#2, C(24A)-(24A)...N(1A), C(24A)-H(24A)...N(1S)#4, C(2B)-H(2BA)...O(11)#5 Table 7.

Table 7. Hydrogen bonds for [Cu(4,4'-DimeBipy)₂(Cl)]₂(ClO₄)₂H₂O.CH₃CN. [\AA and $^\circ$]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(5A)-H(5AA)...Cl(1)#1	0.95	2.96	3.815(4)	150.4
C(8A)-H(8AA)...Cl(1)#1	0.95	2.88	3.697(4)	145.0
C(11A)-H(11A)...O(11)	0.95	2.58	3.294(5)	132.2
C(13A)-H(13A)...Cl(1)	0.95	2.78	3.288(4)	114.6
C(14A)-H(14A)...O1WAa#2	0.95	2.38	3.230(8)	148.4
C(14A)-H(14A)...O1WBb#2	0.95	2.53	3.45(3)	163.5
C(23A)-H(23A)...O(12)#3	0.95	2.54	3.380(6)	147.6
C(24A)-H(24A)...N(1A)	0.95	2.64	3.155(5)	114.7
C(24A)-H(24A)...N(1S)#4	0.95	2.67	3.480(6)	143.4
C(2B)-H(2BA)...O(11)#5	0.95	2.56	3.429(5)	152.0
C(8B)-H(8BA)...Cl(2)#6	0.95	2.98	3.778(4)	142.0
C(2S)-H(2S1)...O(21)	0.91(7)	2.68(7)	3.582(7)	174(6)
C(2S)-H(2S3)...Cl(2)#7	0.93(6)	2.91(6)	3.841(6)	175(5)
O1WAa-H1W2a...Cl(3)	1.08(5)	2.59(5)	3.653(6)	172(5)
O1WAa-H1W2a...O(22)	1.08(5)	2.04(6)	2.999(8)	148(6)
O1WAa-H1W2a...O(23)	1.08(5)	2.24(6)	3.174(8)	145(6)
O1WBb-H1W3b...O(13)	0.85(5)	2.12(6)	2.96(3)	174(12)
O1WBb-H1W3b...O(14)	0.85(5)	2.12(12)	2.64(3)	119(10)
O1WBb-H1W3b...Cl(4)	0.85(5)	2.58(9)	3.35(3)	152(11)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1 #2 -x+2,-y+1,-z+1 #3 x-1,y,z, #4 x-1,y-1,z #5 x,y,z-1 #6 -x+1,-y+1,-z, #7 x+1,y+1,z+1

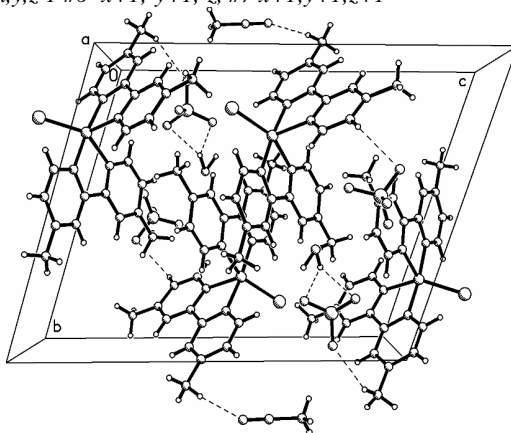


Figure 6. b- axis projection of the crystal structure of [Cu(4,4'-DimeBipy)₂(Cl)]₂(ClO₄)₂H₂O.CH₃CN

Each unit interacts through these strong intramolecular hydrogen bonds and intermolecular bonds Figure 6 leading to the formation of infinite 1D molecular structure. This chain close packing along the *b*-axis of the unit cell gives a dense crystalline packing arrangement Figure 6.

Conclusion

Three mixed-ligand complexes $[\text{Cu}(\text{4,4'}\text{-dimeBipy})_2(\text{N}_3)]_2(\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$, $[\text{Cu}(\text{4,4'}\text{-DimeBipy})_2(\text{NCS})]\text{SCN}$ and $[\text{Cu}(\text{4,4'}\text{-DimeBipy})_2(\text{Cl})]_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$ have been successfully synthesized and the structures elucidated. The distorted square pyramidal complexes experienced lengthening of the bond between the central Cu atom and the donor atoms of the coordinated ligands. Hydrogen bonds in the complexes gave the molecular structure stable crystal packing. The presence of the pseudohalides affect considerably the bond lengths of the complexes when compared with those of the unsubstituted starting complex reported in the literature.

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Supplementary data

CCDC 1471685, 1471686 and 1471687 contain the supplementary crystallographic data for $[\text{Cu}(\text{4,4'}\text{-DimeBipy})_2(\text{N}_3)]_2(\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$, $[\text{Cu}(\text{4,4'}\text{-DimeBipy})_2(\text{NCS})]\text{SCN}$ and $[\text{Cu}(\text{4,4'}\text{-DimeBipy})_2(\text{Cl})]_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$ respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographical Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E- mail: deposit@ccdc.cam.uk.

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