Five-Coordinated Geometries from Molecular Structures to Solutions in Copper(II) Complexes Generated from Polydentate-N-Donor Ligands and Pseudohalides

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Abstract: A novel series of mononuclear five-coordinated pseudohalido-Cu(II) complexes displaying distorted square bipyramidal: [Cu(L1)(NCS)2] (1), [Cu(L2)(NCS)2] (2) and [Cu(L3)(NCS)]ClO4 (5) as well as distorted trigonal bipyramidal: [Cu(isp3 tren)(N3)]ClO4 (3), [Cu(isp3 tren)(dca)]ClO4 (4) and [Cu(tedmmpz)(dca)]ClO4·0.67H2O (6) geometries had been synthesized and structurally characterized using X-ray single crystal crystallography, elemental microanalysis, IR and UV-vis spectroscopy, and molar conductivity measurements. Different N-donor amine skeletons including tridentate: L1 = [(2-pyridyl)-2-ethyl-(3,4-dimethoxy)-2-methylpyridyl]methylamine and L2 = [(2-pyridyl)-2-ethyl-(3,5-dimethyl-4-methoxy)-2-methylpyridyl]methylamine, and tetradentate: L3 = bis(2-ethyl-di(3,5-dimethyl-1H-pyrazol-1-yl)-[2-(3,4-dimethoxy-pyridyl)methyl]amine, tedmpz = tris[(2,3,5-dimethyl-1H-pyrazol-1-yl)ethyl]amine and isp3 tren = tris[(2-isopropylamino)ethyl]amine ligands were employed. Molecular structural parameters such as nature of coligand, its chelate ring size and steric environment incorporated into its skeleton, which lead to adopting one of the two limiting geometries in these complexes and other reported compounds are analyzed and correlated to their assigned geometries in solutions. Similar analysis were extended to other five-coordinated halido-Cu(II) complexes.

Keywords: copper; crystal structure; isothiocyanate; azide; dicyanamide; five-coordinated; UV-vis spectra

1. Introduction

Copper is an essential element for life as it is incorporated into a variety of proteins and metalloenzymes, which occur in animals and plants and required to perform essential metabolic functions. Many of biologically active copper enzymes are utilized for electron transfer reactions,
oxygen transport and oxygenation reactions [1,2]. The deficiency in copper or its high concentration in human tissues may lead to Menkes or Wilson diseases, respectively [3]. Over the last decade, a wide range of copper(II) complexes were demonstrated to be potentially effective as anticancer agents [4–8] and less toxic compared to the currently used platinum-based anticancer drugs [9]. Many of the designed anticancer Cu(II) are coordination compounds containing polyamines as coligands and chloride or bromide groups [5–8,10–12]. In some cases, these halido compounds are unstable in solutions and may undergo solvolysis or aquation with possible stereochemical geometry change [5,7,11,12].

The interaction of pseudohalides (isothiocyanate, NCS\(^-\); azide, N\(_3\)\(^-\); and dicyanamide, dca) with Cu(II) salts in the presence of coligands resulted in the construction of polynuclear compounds with different dimensionality and nuclearity, and coordination polymers (CPs) with diverse topology [13–19]. This was attributed to the high ability of the pseudohalide ions to act as bridging ligands in a variety of bonding modes and mediating the magnetic interaction between Cu\(^{2+}\) centers [17–20], where efficient magnetic transmitting was found in case of the azide bridging compounds [17,19,20]. However, mononuclear pseudohalido-Cu(II) complexes are known to be formed too [21–30] and are very stable in aqueous and common organic solvents [27,28]. The Cu(II) centers in these compounds display variable geometries ranging from four—(square planar and tetrahedral) to six—(octahedral) as well as five-coordinated species. The latter species exist in solutions in equilibrium between the square pyramidal (SP) and trigonal bipyramidal (TBP) geometries as the energy barrier between the two species is very small [31]. Several structural parameters such as steric effect, nature of the chelate ring size (ligand bite) and skeleton of the coordinated coligand were proposed to account for the presence of specific predominant stereochemical geometry [22–24]. Taking into considerations the stability of the pseudohalido- vs. instability of some halido-copper(II) complexes, it is safe to point out that molecular structures do not always provide information about how these halido complexes exist in solution, especially if the halido-Cu(II) compounds persist in solutions [5,7].

Thus, in order to investigate the above parameters that influence the geometry of the five-coordinated Cu(II) species, a novel series of mononuclear pseudohalido complexes derived from N-donors tri- and tetra-dentate amines with different coligand skeletons were synthesized. These include: [Cu(L\(_1\))(NCS)\(_2\)] (1), [Cu(L\(_2\))(NCS)\(_2\)] (2), [Cu(isp\(_3\)tren)(N\(_3\))ClO\(_4\)] (3), [Cu(isp\(_3\)tren)(dca)]ClO\(_4\) (4), [Cu(L\(_3\))(NCS)]ClO\(_4\) (5), [Cu(tedmpza)(dca)]ClO\(_4\)·0.67H\(_2\)O (6) and [Cu(L\(_4\))(dca)]ClO\(_4\)·2H\(_2\)O (7) complexes, where L\(_1\) = [(2-pyridyl)-2-ethyl](3,4-dimethoxy)-2-methylpyridyl]methylamine, L\(_2\) = [(2-pyridyl)- 2-ethyl)-(3,5-dimethyl-4-methoxy)-2-methylpyridyl]methylamine, L\(_3\) = bis(2-ethyl-di(3,5-dimethyl-1H-pyrazol-1-yl)-(2,3,4-dimethoxy)pyridyl)methylamine, L\(_4\) = bis(2-methylpyridyl)-(2-(3,4-dimethoxy)pyridyl)methylamine, isp\(_3\)tren = tris(2-isopropylamino)ethyl]amine and tedmpza = tris[(2,3,5-dimethyl-1H-pyrazol-1-yl)ethyl]amine (Scheme 1). The molecular structures of these complexes were determined and analyzed as function of the index distortion parameters \(\tau\) and correlated to the assigned geometries, which were derived from their visible electronic spectra in solutions. The results are discussed and compared to other related pseudohalido as well as halido compounds in an attempt to predict the predominant five-coordinated geometry in solution and for how far one can rely on this geometrical assignment.
The green azido complex, [Cu(isp3tren)(NCS)2] (L4) was obtained using a similar procedure as that described for the dicyanamido complexes. The isolated complexes were produced in moderate to excellent yields (60–95%). Single crystals suitable for X-ray analysis were obtained either from dilute aqueous-methanol solutions (3, 4) or recrystallization (CH3CN: 1, 2; CH3OH: 6; and H2O: 5). Attempts made to get good crystals of complex 7 failed. All the complexes were characterized by elemental microanalyses, IR and UV-vis spectra and molar conductivity measurements (ΛM in acetonitrile solutions) as well as X-ray single crystals crystallography for complexes 1–6. The molar conductivity of the complexes 3–7 were found to be in the range 147–163 Ω⁻¹·cm²·mol⁻¹, which are in complete agreement with the predicted formulas as 1:1 electrolytic nature [32]. On the other hand, [Cu(L1)(NCS)2] (1) and [Cu(L2)(NCS)2] (2) complexes produced ΛM values of 9 and 11 Ω⁻¹·cm²·mol⁻¹, respectively. These values are fully consistent with their non-electrolytic behavior [32,33]. The complexes are soluble in CH3CN and CH3OH and their solution electronic or molar conductivity, which were measured over four days did not show any sign of solvolysis, geometrical changes, nor degradation.

Scheme 1. Structure formulas of some N-donor ligands used in this study. Tris(2-pyridylmethyl)amine (TPA) was illustrated in the scheme for comparison with other derivatives of the compound.

2. Results and Discussion

2.1. Synthetic Aspects

The interaction of methanolic solutions containing Cu(ClO4)2·6H2O or Cu(NO3)2·3H2O with the tridentate amines L1 or L2 (Scheme 1) in the presence of NH4NCS and the stoichiometric ratios 1:1:1 or 1:1:2 afforded the mononuclear diisothiocyanato complexes [Cu(L1)(NCS)2] (1) and [Cu(L2)(NCS)2] (2), respectively, whereas the reaction of Cu(ClO4)2·6H2O with the tripod tetraamine ligand, L3 resulted in the formation of [Cu(L3)(NCS)]ClO4 (5). Similarly, bluish green complexes [Cu(isp3tren)(dca)]ClO4 (4), [Cu(tedmpza)(dca)]ClO4·0.67H2O (6), and [Cu(L4)(dca)]ClO4·2H2O (7) were obtained from the reactions of methanolic solutions containing Cu(ClO4)2·6H2O and the corresponding tripod ligands isp3tren, tedmpza and L4 (Scheme 1) respectively, with an aqueous solution of Nadca in a 1:1:1 or even 1:1:2 molar ratios. The green azido complex, [Cu(isp3tren)(N3)]ClO4 (3) was obtained using a similar procedure as that described for the dicyanamido complexes. The isolated complexes were produced in moderate to excellent yields (60–95%).
2.2. IR Spectra of the Complexes

The IR spectra of the isothiocyanato compounds 1, 2 and 4 display a strong stretching vibration at 2055, 2054, and 2091 cm\(^{-1}\) respectively, corresponding to the \(\nu_{as}(\text{C}=\text{N})\) frequency. This is most likely consistent with N-bonded isothiocyanate, which in general shows \(\nu_{as} < 2110\) cm\(^{-1}\), whereas the corresponding S-bonded isothiocyanate bonding mode reveals the \(\nu_{as}(\text{C}=\text{N})\) at higher frequencies (>2110 cm\(^{-1}\)) [23,24,34–36]. The azido complex 3 displays a single very strong absorption band at 2055 cm\(^{-1}\) due to the asymmetric stretching vibration, \(\nu_{as}(\text{N}_3)\) of the coordinated mono-dentate azido group [18,26,29]. Three strong bands were detected over the frequency region 2350–2170 cm\(^{-1}\) for the dicyanamido complexes 4 and 6 being comparable to those observed in the free dicyanamide stretching frequencies \([\nu_{as} + \nu_{sym}(\text{C}=\text{N})]\) 2286 cm\(^{-1}\), \(\nu_{as}(\text{C}=\text{N})\) 2232 cm\(^{-1}\) and \(\nu_{sym}(\text{C}=\text{N})\) 2179 cm\(^{-1}\) [37] and indicating monodentate N-nitride dca [27–29]. However, we should mention that the dicyanamido complex 7 displayed four strong bands for the coordinated dca at 2300, 2236, 2176, and 2137 cm\(^{-1}\). In addition the compounds 3–7 reveal a single strong band over the range 1100–1070 cm\(^{-1}\) attributable to the \(\nu(\text{Cl-O})\) stretching vibration of the perchlorate counter ion. The split of this band (1090 and 1067 cm\(^{-1}\)) in 7 is probably due to the reduction of the ClO\(^{-}\) symmetry from Td to C\(_{3v}\) or C\(_{2v}\). The water of crystallization in [Cu(terminal dca)]ClO\(_4\).0.67H\(_2\)O (6) and [Cu(terminal dca)]ClO\(_4\).2H\(_2\)O (7) was detected as a broad band at 3448 and 3435 cm\(^{-1}\) respectively, due to \(\nu_{as}(\text{O-H})\) stretching frequency.

2.3. Description of the Structures

2.3.1. [Cu(L\(^1\))(NCS)\(_2\)] (1), [Cu(L\(^2\))(NCS)\(_2\)] (2) and [Cu(L\(^3\))(NCS)]ClO\(_4\) (5)

The isothiocyanate compounds 1 and 2 form neutral monomeric complexes, whereas 5 crystallizes as a mononuclear complex cation together with perchlorate counter anion. In 1 and 2, the Cu(II) centers are ligated by two terminal \(\text{N}\)-coordinated NCS\(^-\) anions and three donor \(\text{N}\)-atoms of the tri-dentate amine ligands L\(^1\) and L\(^2\), respectively, while in complex cation of 5, the Cu(II) center is ligated by one terminal \(\text{N}\)-coordinated NCS\(^-\) anion and four donor \(\text{N}\)-atoms of the tetra-dentate amine ligand L\(^3\) (Figure 1). The CuN\(_5\) chromophores of the metal centers exhibit distorted and slightly elongated square pyramidal (SP) geometry with \(\tau\)-values of 0.08 for 1, 0.14 for 2, and 0.02 for 5 [38]. In the neutral complexes the apical position is occupied by N-NCS\(^-\), with Cu-N apical bond distances of 2.188(2) and 2.165(7) Å, for 1 and 2, respectively, whereas in 5 the apical position is occupied by N4 of the tetra amine L\(^3\) ligand [Cu-N4 = 2.232(3) Å]. The basal Cu-N bond lengths in the three compounds vary from 1.955(3) to 2.087(3) Å. The central N(amine) donor atoms of L\(^1\), L\(^2\), and L\(^3\) molecules, respectively, are placed trans to the basal N-(NCS) anions, which have the shortest Cu-N bonds [1.955(3)–1.988(6) Å]. The terminal NCS\(^-\) anions have the following bond parameters: N-C: 1.153(3)–1.163(10) Å; C-S: 1.626(4)–1.649 Å; Cu-N-C 149.0(2)–175.0(3)°; N-C-S: 177.9(7)–179.5(4)°.

![Figure 1](image-url). Perspective views of 1 (left), 2 (center) and complex cation of 5 (right). \(\tau\) and \(\phi\) bond angles (°) used for calculation of \(\tau\)-values: 1: N3-Cu-N5 167.20(3); N1-Cu-N4 162.13(9); 2: N3-Cu-N5 168.4(3), N2-Cu-N4 160.3(3); and 5: N6-Cu-N7 163.94(12), N1-Cu-N2 162.46(12).
2.3.2. \([\text{Cu(isp}_3\text{tren})(\text{N}_3)]\text{ClO}_4 (3), [\text{Cu(isp}_3\text{tren})(\text{dca})]\text{ClO}_4 (4), \) and \([\text{Cu(tedmpza)}(\text{dca})]\text{ClO}_4\cdot0.67\text{H}_2\text{O} (6)\)

The mononuclear \([\text{Cu(isp}_3\text{tren})(X)]^+\) complex cations, \([X = \text{N}_3 \text{for 3 and dca for 4}]\) co-crystallize with \(\text{ClO}_4^-\) counter anions. Three crystallographic independent \([\text{Cu(tedmpza)}(\text{dca})]^-\) cations with three \(\text{ClO}_4^-\) counter anions and two solvent water molecules are located in the triclinic unit cell of 6. Each Cu(II) center in compounds 3, 4, and 6 is ligated by one terminal N-coordinated pseudohalide anion and four N-donor atoms of the arms of the tetra-dentate amine ligands (isp3tren or tedmpza) (Figure 2). The CuN5 chromophores of the copper centers exhibit slightly distorted trigonal bipyramidal (TBP) geometry with \(\tau\)-values of 0.78 for 1, 0.77 for 2, and 0.78, 0.89, and 0.82 for Cu1-Cu3 of 6, respectively [38]. The axial positions are occupied by one N-terminal pseudohalide anion and the central N(amine) donor atom of the tetra-dentate molecules, whereas the equatorial positions are occupied by three N-donor atoms of the arms of the isp3tren or tedmpza molecules. The shortest bond distances within each CuN5 polyhedron are observed for the Cu-N(\(\text{N}_3\)) \([1.9735(17) \text{ Å}]\) and Cu-N(dca) \([\text{from 1.951(6) to 1.971(5) Å}]\), while the axial Cu-N(amine) bond distances are in the range from 2.041(3) to 2.097(5) Å. The equatorial Cu-N bond lengths vary from 2.043(6) to 2.2417(17) Å. The terminal azide anion in 3 has N5-N6 and N6-N7 bond distances of 1.193(3) and 1.163(5) Å, and Cu-N5-N6 and N5-N6-N7 bond angles of 130.37(14) and 176.3(2)°, respectively. The terminal dca anions in 4 and 6 have the following bond parameters: C-N(nitrite): from 1.107(10) to 1.162(8) Å; C-N(amine): from 1.290(9) to 1.339(11) Å; Cu-N-C: from 162.5(6) to 173.6(6)°; N-C-N: from 163.5(9) to 175.9(8)°; and C-N-C: from 116.1(8) to 122.1(4)°.

Figure 2. Perspective views of complex cations of 3 (left), 4 (center), and 6 (right). \(\theta\) and \(\phi\) bond (°) used for calculation of \(\tau\)-values: 3: N5-Cu1-N1 179.28(7); N2-Cu1-N3 132.54(6); 4: N5-Cu1-N1 176.21(14), N2-Cu1-N4 129.85(14); 6: N1-Cu1-N8 176.0(2), N3-Cu1-N7 128.2(2); N11-Cu2-N18 178.4(2), N15-Cu2-N17 125.3(2); and N21-Cu3-N28 176.7(2), N23-Cu3-N27 127.8(2).

In 6, the three complex cations differ mainly in the torsion around the dca ligation [torsion angles: Cu1-N8--N9--N10 = 116.87°; Cu2-N18--N19--N20 = 47.37°; Cu3-N28--N29--N30 = 104.94°]. Furthermore, only dca donor atom N30 of complex cation of Cu3 is involved in a hydrogen bond of type O-H--O to water molecule O13, which forms also a hydrogen bond of type O-H--O to perchlorate counter anion of Cl2. The second water molecule O14 forms only hydrogen bonds of type O-H--O to water molecule O13 and perchlorate counter anion of Cl3 (see packing plot Figure S6, and Table S4, Supplementary Materials).

2.4. \(\text{UV-Vis Spectra of the Complexes}\)

The acetonitrile electronic spectra of the Cu(II) complexes 1–7 can be classified into two categories:
(1) Complexes 1 and 2, which were derived from tridentate ligands L1 and L2 exhibit a single broad absorption around 676 nm.
(2) Complexes 3–7 revealed a shoulder or relatively weak band over the region 630–740 nm and a broad band over the wavelength region 840–940 nm.
In addition, the very strong intense band located around 390 nm for compounds 1, 2, 5 and 6, and at 350 nm in 7 can be assigned to ligand-metal charge transfer transition (LMCT). The visible spectral features observed in the two categories of complexes are consistent with five-coordinated Cu(II) geometries. In general, Cu\textsuperscript{2+} in square pyramidal geometry (SP) exhibits broad band in the visible region (590–780 nm), which occasionally may or may not be associated with a low-energy shoulder at \( \lambda > 800 \) nm (spin forbidden), whereas trigonal bipyramidal (TBP) are known to display a single \( d-d \) band at \( \lambda > 800 \) nm with a high-energy shoulder in the visible region [39]. Therefore, based on this criterion, the acetonitrile visible spectral data of the complexes under investigation are consistent with SP geometry in complexes 1 and 2 [25,40], whereas TBP environment seems to be dominating in the second category of complexes 3–7 coordinated to tripodal tetraamine coligands (L\textsubscript{3}, L\textsubscript{4}, isp\textsubscript{3}tren, tedmpza; Scheme 1) [41]. It is important to point out that the intensity of band at \( \lambda > 800 \) nm in TBP geometries should be higher than the shoulder or the band located at \( \lambda < 800 \) nm (small intense maxima). However, it should be emphasized that in most cases, the complexes may exhibit intermediate geometries which are slightly distorted from the ideal SP or TBP.

2.5. Molecular vs. Solution Structures in Five-Coordinated Cu(II) Complexes

Five-coordinated metal(II) complexes, especially when the central metal ion is Cu(II), Co(II), or Zn(II) are quite known to crystallize in two stereochemical environments around the central M\textsuperscript{2+} ion namely square pyramidal (SP) and trigonal bipyramidal (TBP) (Figure 3) because the energy barrier between the two possible limiting geometries is rather small [32]. Several factors were considered to contribute to this phenomenon such as the nature of the central metal ion, chelate ring size, and coligand’s skeleton as well as the steric substituent effect incorporated into its structure. These factors play crucial roles in adopting one of the two geometries. From the molecular structure point of view, it is possible to quantify the extent of distortion of the metal polyhedron through the evaluation of the structural index parameter (\( \tau \)), which is defined as the ratio between the two basal angles \( \theta \) and \( \phi \) in the given five-coordinated complex, \( \tau = (\theta - \phi)/60 \), where \( \theta \geq \phi \). A perfect TBP is associated with \( \phi = 120^\circ \) and \( \theta = 180^\circ \), leads to \( \tau = 1 \), whereas in an ideal SP geometry \( \theta = \phi = 180^\circ \) leading to \( \tau = 0 \) [38]. In real SP structures, the metal ion is always located out of the equatorial plane towards the axial bond and the resulting C\textsubscript{4v} geometry is still be characterized by \( \tau \approx 0 \left( \theta \approx \phi < 180^\circ \right) \). In the solid state, one of the two conformations is isolated as a predominant geometrical isomer. However, in solutions the situation is different and it is not necessary that the molecular structure, which isolated persists in solution.

![Figure 3](image_url)

**Figure 3.** Topological transformation between square pyramidal (SP) and trigonal bipyramidal (TBP) geometries.

This section is devoted to consider the molecular and solution structures of the mononuclear pseudohalide-Cu(II) five-coordinated complexes 1–6 together with some other related compounds, which are also mononuclear and their structures were determined in both the solid and solution states. This comparison will allow us to analyze the structural parameters leading to the isolation of a specific geometrical conformation (TBP vs. SP). Therefore, a number of these compounds were compiled in
Table 1 together with their corresponding $\tau$ values. Furthermore, the visible spectra of the same series of compounds in solutions are collected in Table 2. Comparing the molecular and solution structures should provide some information about the validity of the predicted geometry in solutions and to what extent one can rely on the structural results in solutions.

Table 1. Geometry and distortion parameter ($\tau$) in mononuclear five-coordinated pseudohalido-copper(II) complexes derived from N-donor ligands in the solid states $^a$.

| Complex                                      | $\tau$ Value | Geometry $^b$ | Ref.          |
|----------------------------------------------|--------------|---------------|---------------|
| $[\text{Cu}(L^1)(\text{NCS})_2]$             | (1)          | 0.08          | dist. SP      | This work     |
| $[\text{Cu}(L^2)(\text{NCS})_2]$             | (2)          | 0.14          | dist. SP      | This work     |
| $[\text{Cu}(\text{bdmpzpy})(\text{NCS})_2]$  | (8)          | 0.25          | dist. SP      | [23]          |
| $[\text{Cu}(\text{Mebedmpz})(\text{NCS})_2]$| (9)          | 0.06          | dist. SP      | [22]          |
| $[\text{Cu}(\text{Bzbedmpz})(\text{NCS})_2]$| (10)         | 0.26          | dist. SP      | [22]          |
| $[\text{Cu}(\text{DPA})(\text{NCS})(\text{ClO}_4)]$ | (11)     | 0.21          | dist. SP      | [23]          |
| $[\text{Cu}(\text{mpipy})(\text{NCS})_2]$   | (12)         | 0.11          | dist. SP      | [42]          |
| $[\text{Cu}(\text{mpiq})(\text{NCS})_2]$   | (13)         | 0.33          | dist. SP      | [42]          |
| $[\text{Cu}(\text{pzdepy})(\text{NCS})\text{ClO}_4]$ | (14) | 0.11          | dist. SP      | [43]          |
| $[\text{Cu}(\text{Me}_3\text{dpt})(\text{NCS})_2]^c$ | (15) | 0.37, 0.49 | dist. SP; intermed. | [40] |
| $[\text{Cu}(\text{bedmpz})(\text{NCS})_2]^c$  | (16)         | 0.24, 0.46    | dist. SP; intermed. | [24] |
| $[\text{Cu}(\text{tepza})(\text{NCS})\text{ClO}_4]$ | (17) | 0.47           | Intermed.     | [25]          |
| $[\text{Cu}(\text{bdmpe})(\text{NCS})\text{ClO}_4]$ | (18) | 0.17           | dist. SP      | [30]          |
| $[\text{Cu}(L^3)(\text{NCS})\text{ClO}_4]$  | (5)          | 0.02          | SP            | This work     |
| $[\text{Cu}(\text{cyclen-tpam})(\text{NCS})\text{ClO}_4\cdot3\text{H}_2\text{O}]$ | (19) | 0.00           | SP            | [23]          |
| $[\text{Cu}(L^3)(\text{NCS})\text{ClO}_4]$  | (20)         | 0.43          | dist. SP      | [44]          |
| $[\text{Cu}(L^5)(\text{N}_3)\text{ClO}_4]^c$ | (21)         | 0.57, 0.65, 0.69 | dist. TBP | [44]          |
| $[\text{Cu}(\text{dpq})_2(\text{N}_3)\text{ClO}_4]$ | (22) | 0.22           | dist. SP      | [45]          |
| $[\text{Cu}(\text{pbpd})(\text{N}_3)\text{PF}_6]$ | (23) | 0.60           | dist. SP      | [46]          |
| $[\text{Cu}(\text{pfbd})(\text{N}_3)\text{ClO}_4]$ | (24) | 0.50           | Intermed.     | [46]          |
| $[\text{Cu}(\text{Me}_3\text{tren})(\text{N}_3)\text{ClO}_4]$ | (25) | 0.80           | dist. TBP     | [29]          |
| $[\text{Cu}(\text{isp}_3\text{tren})(\text{N}_3)\text{ClO}_4]$ | (3) | 0.78           | dist. TBP     | This work     |
| $[\text{Cu}(\text{pdpa})(\text{N}_3)\text{ClO}_4]$ | (26) | 0.60           | dist. TBP     | [29]          |
| $[\text{Cu}(\text{TPA})(\text{N}_3)\text{ClO}_4]$ | (27) | 0.91           | dist. TBP     | [41]          |
| $[\text{Cu}(\text{BA})(\text{N}_3)\text{ClO}_4]$ | (28) | 0.65           | dist. TBP     | [47]          |
| $[\text{Cu}(\text{F}_5\text{BA})(\text{N}_3)\text{ClO}_4\cdot3\text{SO}_3]^c,d$ | (29) | 0.73; 0.68; 0.50; 0.61; 0.31 | dist. TBP; dist. SP, intermed. | [47] |
| $[\text{Cu}(\text{pmap})(\text{N}_3)\text{ClO}_4]$ | (30) | 0.10           | dist. SP      | [43]          |
| $[\text{Cu}(\text{tedmpz})(\text{N}_3)\text{ClO}_4]$ | (31) | 0.06           | dist. SP      | [23]          |
| $[\text{Cu}(\text{trpn})(\text{N}_3)\text{ClO}_4]$ | (32) | 0.23           | dist. SP      | [48]          |
| $[\text{Cu}(\text{medien})(\text{dca})_2]$ | (33) | 0.23           | dist. SP      | [29]          |
| $[\text{Cu}(\text{pzdepy})(\text{dca})\text{ClO}_4]$ | (34) | 0.24           | dist. SP      | [28]          |
| $[\text{Cu}(\text{tren})(\text{dca})\text{ClO}_4]$ | (35) | 0.87           | dist. TBP     | [27]          |
In contrast, the corresponding azido-(cyclen-tmpa) ligands show very high tendency to adopt SP geometry regardless the chelate ring sizes and the crystal packing.

Table 1. Cont.

| Complex                                      | τ Value | Geometry | Ref.    |
|----------------------------------------------|---------|----------|---------|
| [Cu(isp3tren)(dca)]ClO₄                        | (4)     | 0.77     | dist. TBP | This work |
| [Cu[TPA](dca)]ClO₄                            | (36)    | 0.95     | dist. TBP | [28]      |
| [Cu(tepza)(dca)]ClO₄                          | (37)    | 0.21     | dist. SP  | [28]      |
| [Cu(tepza)(dca)]ClO₄                          | (38)    | 0.61, 0.63 | dist. TBP | [25]      |
| [Cu(tedmpza)(dca)]ClO₄, 0.67H₂O              | (6)     | 0.79, 0.89, 0.82 | dist. TBP | This work |

a Ligand abbreviations: L¹ = (2-pyridyl)-2-ethyl-(3,4-dimethoxy)-2-methylpyridyl]methylamine, L² = (2-pyridyl)-2-ethyl-(3,5-dimethyl-4-methoxy)-2-methylpyridyl]methylamine, L³ = bis(2-ethyl-di(3,5-dimethyl-1H-pyrazol-1-y1)]-2-(3,4-dimethoxy)pyridylmethyl]amine, L⁴ = bis(2-methylpyridyl)-2-(3,4-dimethoxy)pyridylmethyl]amine, L⁵ = 1-[N,N'-bis(1-pyridin-2-yl-ethylidene)-2,2-dimethylpropane-1,3-diamine, bedmpza = bis[2-(di-2,5-dimethyl-1-pyrazolyl)-ethyl]amine, Mebedmpza = N-methyl-bis(3,5-dimethyl-2-(pyrazol-1H-yl)ethyl]amine, Bzbedmpza = N-benzyl-bis(3,5-dimethyl-2-(pyrazol-1H-yl)ethyl]amine, bdmpzy = 2,6-bis(2,5-dimethyl-1H-pyrazol-1-y1)methyl]pyridine, pmbedien = N,N,N',N''-pentamethyldiethylenetriamine, DPA = bis(2-methylpyridyl)amine, Me₂dpt = bis(N-methyl-3-aminopropyl)methylamine, mpipy = N-methyl-N-(2-pyridyl)methyl]piperazine, mpiq = N-methyl-N-(2-quinoilyl)methyl]piperazine, pdpa = N-(3-aminopyrrolino)-N,N-bis(2-pyridyl)amine, pxdepy = N,N-bis[2-(2-pyridyl)ethyl]piperazine, tren = tris(2-aminomethyl)amine, Me₃tren = tris(2-aminomethyl)amine, isp = tris[(2-isopropyl-aminomethyl)amine, trpn = tris(3-aminopropyl)amine, tspa = tris[(2-aminomethyl)ethyl]amine, tespza = tris(2-ethyl-di(3,5-dimethyl-2-(pyrazol-1H-yl)ethyl)amine, dpq = dipyrido[3,2-f:2,3-h]quinoxaline, pbpd = N,N'-bis(pyridin-2-yl)benzylidene)-2,2-dimethylpropane-1,3-diamine, pdpy = N,N'-bis(pyridin-2-yl)-formylidene)butane-1,4-diamine, BA = 6-(bis(pyridin-2-yl)methyl)amine)methyl)-N-((phenyl) methyl]pyridin-2-amino, F₃BA = 6-(bis(pyridin-2-yl)methyl)amine)methyl)-N-((perfluorophenyl) methyl]pyridin-2-amino. b dist. = distorted. Intermed. = intermediate. c two or more molecules are in the unit cell. d complex is severely disordered. Note: As in the title compounds 1–6 the CuN₅ complexes all 10 valence angles of N-Cu-N have different values, the maximum angle is always the θ angle, and next largest angle is always the φ angle.

Inspection of the data given in Table 1 reveals that five-coordinated isothiocyanato-Cu(II) complexes 1, 2 and 8–20, which were derived from linear tridentate, tripodal tetra- or cyclic-tetradentate (cyclen-tmpa) ligands show very high tendency to adopt SP geometry regardless the chelate ring sizes (five or six). In contrast, the corresponding azido 3, 25, and 27, and the dicyanamido series 4, 8, and 36 constructed from tripodal tetradentate ligands with all compounds displaying five-membered chelate rings (tren, Me₃tren, isp₃tren, TPA) indicate more preference for TBP geometry. This stereochemical structure changes to SP as the number of six-membered rings increases as this was the case on going from TPA (complexes 27 and 36 with τ values of 0.91 and 0.95, respectively) to trimap or tepa in compounds 30 and 37 as well as in [Cu(tedmpza)(N₂)ClO₄ (31) or from tren to trpn in complexes 35 and 32, respectively. Most likely this is attributed to the flexibility of the six-membered chelate rings. Similar SP geometry was also observed when steric effect at the coordinated amines are fully alkylated as in [Cu(pmedien)(dca)]ClO₄ (33). Moreover, moderate substituents into the pyridyl groups of TPA, especially at position 6 results in increasing the distortion of the TBP geometry observed in TPA complexes (see complexes 28: τ = 0.65 and 29: τ = 0.65 and 0.73, 0.68; 0.50; 0.61; 0.31, [47]). However, we should mention that some pronounced deviations were found in the azido compound 31 and its corresponding dicyanamido, [Cu(tedmpza)(dca)]ClO₄ 0.67H₂O (6) and in related tris pyrazolyl, [Cu(tepza)(dca)]ClO₄ (38) (based on the above analysis both are expected to exhibit SP). These deviations may result from the crystal packing.
The question now which class of compounds can retain their geometries in solutions? To provide a satisfactory answer to this question, the solution visible electronic spectra of the compounds shown in Table 1 are collected in Table 2 with predicted predominant geometries based on the analysis provided in Section 2.4. Probably, we should mention that the complexes 1–7 were shown to be very

| Complex                          | Solvent     | $\lambda_{\text{max}}$, nm ($\epsilon_{\text{max}}, \text{M}^{-1} \cdot \text{cm}^{-1}$) | Predicted Geometry | Ref.                        |
|---------------------------------|-------------|---------------------------------------------------------------------------------|--------------------|-----------------------------|
| [Cu(lL)$^1$](NCS)$_2$           | (1) CH$_3$CN | 676 (190)                                                                      | dist. SP           | This work                   |
| [Cu(lL)$^2$](NCS)$_2$           | (2) CH$_3$CN | 676 (196)                                                                      | dist. SP           | This work                   |
| [Cu(bdmmpzpy)(NCS)$_2$]         | (8) CH$_3$OH | 670 (sat)                                                                       | dist. SP           | [23]                        |
| [Cu(Mebedmpzza)(NCS)$_2$]       | (9) CH$_3$CN | 731 (155, br)                                                                   | dist. SP           | [22]                        |
| [Cu(Bzbedmpzza)(NCS)$_2$]       | (10) CH$_3$CN| 704 (155, br)                                                                   | dist. SP           | [22]                        |
| [Cu(pmpy)(NCS)$_2$]             | (12) CH$_3$CN| 729 (288)                                                                       | dist. SP           | [42]                        |
| [Cu(impy)(NCS)$_2$]             | (13) CH$_3$CN| 775 (230)                                                                       | dist. SP           | [42]                        |
| [Cu(pzdepy)(NCS)$_2$]           | (14) H$_2$O  | 591 (304)                                                                       | dist. SP           | [43]                        |
| [Cu(Meypdp)(NCS)$_2$]           | (15) CH$_3$CN| 686 (204), 932 (141)                                                            | dist. SP           | [40]                        |
| [Cu(bedmpzza)(NCS)$_2$]         | (16) CH$_3$CN| 725 (149)                                                                       | dist. SP           | [24]                        |
| [Cu(tpzpa)(NCS)$_2$]            | (17) CH$_3$CN| 704 (174, br)                                                                   | dist. SP           | [25]                        |
| [Cu(bmpa)(NCS)$_2$]             | (18) CH$_3$CN| 663 (174)                                                                       | dist. SP           | [30]                        |
| [Cu(lL)$^3$](NCS)ClO$_4$        | (5) CH$_3$CN | ~630 (sh), ~940 (76)                                                             | dist. SP           | This work                   |
| [Cu(cyclen-tpam)(NCS)ClO$_4$3$H_2$O | (19) H$_2$O | 623 (435)                                                                       | dist. SP           | [23]                        |
| [Cu(lL)$^3$](NCS)ClO$_4$        | (20) CH$_3$CN| 720 (203)                                                                       | dist. SP           | [44]                        |
| [Cu(lL)$^4$](N$_3$)ClO$_4$      | (21) CH$_3$CN| 383 (155)                                                                       | dist. SP           | [44]                        |
| [Cu(dpdp)(N$_3$)ClO$_4$]        | (22) DMSO    | 680 (110), 1050 (sh)                                                             | dist. SP           | [45]                        |
| [Cu(bpdb)(N$_3$)PF$_6$]         | (23) MeOH    | 718                                                                              | dist. SP           | [46]                        |
| [Cu(bpdb)(N$_3$)]ClO$_4$        | (24) MeOH    | 720                                                                              | dist. SP           | [46]                        |
| [Cu(Me$_3$trien)(N$_3$)ClO$_4$]  | (25) H$_2$O  | 665 (~162), 835 (300, br)                                                       | dist. TBP          | [29]                        |
| [Cu(isps tren)(N$_3$)ClO$_4$]   | (3) CH$_3$CN | 695 (364, br), 870 (397, br)                                                    | dist. TBP          | This work                   |
| [Cu(dpda)(N$_3$)ClO$_4$]        | (26) H$_2$O  | 656 (132, sh), 852 (200)                                                        | dist. TBP          | [29]                        |
| [Cu(TPA)(N$_3$)ClO$_4$]         | (27) CH$_3$OH| ~650, 836 (201)                                                                 | dist. TBP          | [41]                        |
| [Cu(BA)(N$_3$)ClO$_4$]          | (28) CH$_3$CN| 650, ~880                                                                       | ~dist. TBP         | [47]                        |
| [Cu(P$_2$BA)(N$_3$)ClO$_4$]     | (29) CH$_3$CN| 655, ~870                                                                       | ~dist. TBP         | [47]                        |
| [Cu(mpmap)(N$_3$)]ClO$_4$       | (30) H$_2$O  | 634 (268)                                                                       | dist. SP           | [43]                        |
| [Cu(tedmpzza)(N$_3$)]ClO$_4$    | (31) CH$_3$CN| 713 (334, br)                                                                    | dist. SP           | [23]                        |
| [Cu(trpn)(N$_3$)ClO$_4$]        | (32) H$_2$O  | 685 (118), 900 (sh)                                                              | dist. SP           | [48]                        |
| [Cu(trpn)(N$_3$)ClO$_4$]        | (33) DMSO    | 670 (275), 920 (sh)                                                              | dist. SP           | [48]                        |
| [Cu(1pmdien)cdca]ClO$_4$        | (34) H$_2$O  | 638 (265)                                                                       | dist. SP           | [29]                        |
| [Cu(gzedepy)cdca]ClO$_4$        | (35) H$_2$O  | 591 (304)                                                                       | dist. SP           | [28]                        |
| [Cu(tren)cdca]ClO$_4$           | (36) CH$_3$CN| 665, 828                                                                         | dist. TBP          | [27]                        |
| [Cu(isps tren)cdca]ClO$_4$      | (4) CH$_3$CN | ~660 (sh), 837 (397, br)                                                         | dist. TBP          | This work                   |
| [Cu(TPA)cdca]ClO$_4$            | (36) H$_2$O  | ~650, 822 (239)                                                                  | dist. TBP          | [28]                        |
| [Cu(tepca)cdca]ClO$_4$          | (37) H$_2$O  | 650 (114), ~739 (sh)                                                             | dist. SP           | [28]                        |
| [Cu(tepca)cdca]ClO$_4$          | (37) CH$_3$OH| 640 (187)                                                                        | dist. SP           | [28]                        |
| [Cu(tepca)cdca]ClO$_4$          | (37) CH$_3$CN| 645 (217)                                                                        | dist. SP           | [28]                        |
| [Cu(tepca)cdca]ClO$_4$          | (37) CH$_3$NO$_2$ | 640 (229)                      | dist. SP           | [28]                        |
| [Cu(tepca)cdca]ClO$_4$          | (38) H$_2$O  | 676 (93, br)                                                                     | dist. SP           | [25]                        |
| [Cu(tedmpzza)cdca]ClO$_4$0.6H$_2$O | (6) CH$_3$CN | ~730 (90, sh), ~940 (110, br)                                                    | dist. TBP          | This work                   |
| [Cu(lL)$^4$](dcda)ClO$_4$2H$_2$O | (7) CH$_3$CN | ~665 (sh), 880 (256, br)                                                         | dist. TBP          | This work                   |

Transferring the compound of which its molecular structure was determined into solution is a complicated issue due to possible solvolysis, stereochemical change or decomposition of the complex. The question now which class of compounds can retain their geometries in solutions? To provide a satisfactory answer to this question, the solution visible electronic spectra of the compounds shown in Table 1 are collected in Table 2 with predicted predominant geometries based on the analysis provided in Section 2.4. Probably, we should mention that the complexes 1–7 were shown to be very
stable in common organic solvents for several days. Similar behavior was also reported in complexes [Cu(trpn)(N₃)]ClO₄ (32), [Cu(tepa)(dca)]ClO₄ (37), and [Cu(tren)(dca)]ClO₄ (35) [27,28,48].

Inspection of the data in Table 2, and the corresponding molecular structures given in Table 1, surprisingly indicate complete agreement between the predicted geometries in solution and the molecular structures. This finding means we can rely with confidence that the determined molecular structures in five-coordinated pseudohalido-Cu(II) complexes are retained in solutions without any stereochemical change.

Since many of the halido-Cu(II) complexes are now extensively used to mimic biological systems, especially those derived from tripodal and linear tetraamine coligands (N₄), [Cu(N₄)X]⁺ in DNA cleavage and the cytotoxicity studies as potential anticancer agents [4–8,49–52], it is worthwhile to shed the light on the behavior of this class of compounds in solutions in order check the validity of geometrical structures at the two levels. The data compiled in Table 3 reveals that increasing the steric crowding at the TPA through successive methylation at the 6th position of the pyridyl groups resulted in the conversion from perfect TBP geometry as in [Cu(TPA)Cl]⁺ (39) to distorted SP in [Cu(6-MeTPA)Cl]⁺ (42), and to intermediate geometry in the most sterically hindered [Cu(6-Me₃TPA)Cl]⁺ complex ion (Table 3: compounds 42–46), a result which was unexpected. Probably, this behavior was enhanced when more substituents were incorporated into the TPA-pyridyl group as this was seen in complexes 55–58, where the TBP is becoming more stabilized [8]. The same trend was observed in the quinolyl derivatives of TPA: [Cu(BPQA)Cl]⁺ and [Cu(BQPA)Cl]⁺, where geometry changes to dist. SP and then to dist. TBP in the latter case (compounds 51–54). Moreover, SP geometries seem to be the most preferable species with bidentate (L⁹), linear tri-(L⁸) and tetra-dentate (L¹⁰) ligands as these were the cases of complexes 61–63 [49–51].

**Table 3.** The molecular structure, the distortion index parameter (τ), the visible spectral absorption bands of mononuclear five-coordinated halido-Cu(II) complexes a in acetonitrile solutions and the assigned geometry.

| Complex | τ Value | Geometry | λₘₐₓ, nm (εₘₐₓ, M⁻¹cm⁻¹) | Assigned Geometry | Ref. |
|---------|---------|----------|--------------------------|------------------|-----|
| [Cu(TPA)Cl]ClO₄·H₂O b,c | 0.98, 0.94 | TBP | ~730 (sh), 950 (br) | dist TBP | [52] |
| [Cu(TPA)Cl]ClO₄·H₂O b,c | 1.0 | TBP | 962 (210), 632 (88, sh) | TBP | [53,54] |
| [Cu(TPA)Cl]PF₆ | 0.91 | dist. TBP | 710 (sh), 872 | dist. TBP | [54] |
| [Cu(6-MeTPA)Cl]PF₆ | 0.12 | dist. SP | ~670 (sh), 885 (132, br) | dist SP | [8] |
| [Cu(6-MeTPA)Cl]ClO₄ c | 0.16, 0.24 | dist. SP | - | - | [53] |
| [Cu(6-Me₂TPA)Cl]PF₆ | 0.13 | dist. SP | ~700 (sh), 900 (159, br) | dist TBP | [8] |
| [Cu(6-Me₂TPA)Cl]ClO₄ | 0.07 | SP | - | - | [55] |
| [Cu(6-Me₃TPA)Cl]ClO₄ | 0.43 | Intermed. | - | - | [55] |
| [Cu(BPQA)Cl]ClO₄ | 0.16 | dist. SP | 639 (192), 898 (sh, 23) | dist SP | [56] |
| [Cu(BQPA)Cl]PF₆ | 0.64 | dist. TBP | ~660 (sh), 880 (141, br) | dist TBP | [8] |
| [Cu(BPQA)Cl]ClO₄ | 0.32 | dist. SP | ~700 (sh), 900 (159, br) | dist TBP | [8] |
| [Cu(BQPA)Cl]PF₆ | 0.32 | dist. SP | ~700 (sh), 880 (141, br) | dist TBP | [8] |
| [Cu(L⁹)Cl]ClO₄ | 0.96 | dist. TBP | ~700, ~850 (sh), 970 (355) | dist TBP | [8] |
| [Cu(L¹⁰)Cl]ClO₄ | 0.86 | dist. TBP | ~715 (sh), 960 (230, br) | dist TBP | [8] |
The measurements were performed using Mettler Toledo Seven Easy conductometer (Columbus, OH, USA) and calibration was determined by the aid of 1413 µS/cm conductivity standard. Elemental microanalyses were carried out by Atlantic Microlaboratory (Norcross, GA, USA).

### 3. Materials and Methods

#### 3.1. Materials and Physical Measurements

*N-Methyl-N-(2-pyridyl)ethyl)amine was purchased from Maybridge, Belgium and tris[2-isoptopylamino)ethyl]amine from Aldrich. 3,4-Dimethoxy-2-chloromethylpyridine, 3,5-dimethyl-4-methoxy)-2-chloromethylpyridine, bis(2-methylpyridyl)amine, bis(2-chloroethyl)-amine and 3,5-dimethylpyrazole were purchased from TCI-America (Portland, OR, USA). All other materials were reagent grade quality. Infrared spectra were recorded on a Cary 630 (ATR) spectrometer (Santa Clara, CA, USA) or JASCO FT/IR-480 plus spectrometer (Oklahoma City, OK, USA) using KBr pellets. Electronic spectra were recorded using Agilent 8453 HP diode UV-vis Spectrophotometer (Santa Clara, CA, USA). The molar conductivity of a solution sample was determined from \( \Lambda_M = (1.0 \times 10^3) \kappa/[Cu] \), where \( \kappa \) is the specific conductance and [Cu] is the molar concentration of the complex. The measurements were performed using Mettler Toledo Seven Easy conductometer (Columbus, OH, USA) and calibration was determined by the aid of 1413 µS/cm conductivity standard. Elemental microanalyses were carried out by Atlantic Microlaboratory (Norcross, GA, USA).
Caution! Salts of perchlorate and azide as well as their metal complexes are potentially explosive and should be handled with great care and in small quantities.

3.2. Synthesis of the Compounds

Synthesis of the organic ligands: The compounds [(2-pyridyl)-2-ethyl-(3,4-dimethoxy)-2-methylpyridyl]methylamine (L1) and [(2-pyridyl)-2-ethyl-(3,4-dimethoxy)-2-methylpyridyl]-methylamine (L2) [59], [bis(3,5-dimethyl-ethyl-pyrazol-1H-1-yl)-(3,4-dimethoxy-2-methylpyridyl)amine (L3) [60], [bis(2-methylpyridyl)-(3,4-dimethoxy-2-methylpyridyl)]-amine, (L4) [8] and tris(3,5-dimethyl-ethyl-1H-pyrazol-1-yl)amine (tedmpza) [61,62] were prepared and characterized according to the published procedures.

Synthesis of [Cu(L1)(NCS)2] (1): To a mixture containing [(2-pyridyl)-2-ethyl-(3,4-dimethoxy)-2-methylpyridyl]methylamine, L1 (0.145 g, 0.50 mmol) and Cu(ClO4)2·6H2O (0.190 g, 0.5 mmol) or Cu(NO3)2·3H2O (0.122 g, 0.50 mmol) dissolved in MeOH (20 mL) NH4NCS (0.076 g, 1.0 mmol) was added. The resulting green solution was heated for 5 min, filtered through celite and then allowed to stand at room temperature. After four days, the precipitate formed was collected by filtration and recrystallized from CH2CN to afford green single crystals suitable for X-ray analysis (yield: 0.215 g, 92%). Characterization: Anal. Calcd. for C18H21CuN2O2S2 (467.06 g/mol): C, 46.29; H, 4.53; N, 14.99. Found: C, 46.49; H, 4.47; N, 15.00%. Selected IR bands (ATR, cm⁻¹): 2979 (vw), 2931 (vw), 2879 (vw), 2835 (vw) ν(C-H); 2055 (vs) νas(N=C) (NCS⁻); 1608 (s), 1496 (s), 1444 (s), 1362 (m), 1304 (s), 1231 (s), 1172 (m), 1069 (s), 1000 (s), 902 (m), 820 (s), 787 (m), 769 (vs), 733 (s). UV-vis (CH3CN), λmax, nm (εmax, cm⁻¹ M⁻¹): 385 (1180), 769 (vs).

Synthesis of [Cu(L2)(NCS)2] (2): To a mixture containing [(2-pyridyl)-2-ethyl-(3,5-dimethyl-4-methoxy)-2-methylpyridyl]methylamine, L2 (0.140 g, 0.50 mmol) and Cu(ClO4)2·6H2O (0.190 g, 0.5 mmol) dissolved in MeOH (20 mL) NH4NCS (0.076 g, 1.0 mmol) was added. The resulting green solution was heated for 5 min, filtered and allowed to crystallize at room temperature. After two days, the produced precipitate was collected by filtration and recrystallized from CH3CN to afford green single crystals suitable for X-ray analysis (yield: 0.178 g, 77%). Characterization: Anal. Calc. for C19H23CuN2O2S2 (465.09 g/mol): C, 49.07; H, 4.08; N, 15.06. Found: C, 49.26; H, 4.99; N, 15.13%. Selected IR bands (KBr, cm⁻¹): 3003 (vw), 2919 (vw), 2872 (vw), ν(C-H); 1606 (m), 1489 (m), 1475 (m), 1442 (m), 1268 (m), 1110 (m), 1012 (m), 999 (m), 904 (w), 880 (w), 769 (vs). UV-vis (CH3CN): λmax, nm (εmax, cm⁻¹ M⁻¹): 392 (1214), 676 (196). ΛM (CH3CN) = 11 Ω⁻¹·cm²·mol⁻¹.

Synthesis of [Cu(isp3tren)(N3)]ClO4 (3): To a mixture containing of Cu(ClO4)2·6H2O (0.190 g, 0.5 mmol) and tris(2-isopropylamino)ethylamine dissolved in 10 mL MeOH), an aqueous solution of NaN3 (0.033 g, 0.5 mmol in 5 mL H2O) was added dropwise. The resulting green solution was heated for 5 min, filtered through celite and allowed to stand at room temperature. After 3 days, the shiny green crystals which separated were collected by filtration, washed with propan-2-ol, ether and dried in air (overall yield: 0.210 g, 88%). Characterization: Anal. Calc. for C32H36CuN2O6S (MM = 777.49 g/mol): C, 37.73; H, 7.60; N, 20.53%. Found: C, 37.80; H, 7.69; N, 20.64%. Selected IR bands (ATR, cm⁻¹): 3269 (m), 3215 (m) ν(N-H); 2974 (w), 2879 (w) ν(C-H); 2055 (vs) νas(N3); 1067 (vs) ν(Cl-O) (ClO4⁻). UV-vis in CH3CN: λmax in nm (εmax, M⁻¹·cm⁻¹): 695 (364, vbr), 870 (397, b). ΛM (CH3CN) = 157 Ω⁻¹·cm²·mol⁻¹.

Synthesis of [Cu(isp3tren)(dca)]ClO4 (4): The complex was isolated as tiny blue single crystals after two days using a procedure similar to that described for complex 3, except NaOCl was used instead of sodium azide (overall yield: 0.196 g, 78%). Characterization: Anal. Calc. for C57H38CuN2O6S (MM = 901.51 g/mol): C, 40.71; H, 7.24; N, 19.55%. Found: C, 40.04; H, 7.32; N, 19.76%. Selected IR bands (ATR, cm⁻¹): 3263 (w), 3228 (m) ν(N-H); 2988 (m), 2942 (m), 2885 (m) ν(C-H); 2301 (s), 2238 (s), 2172 (vs) νas(N=C) (dca); 1100 (vs, b) ν(Cl-O) (ClO4⁻). UV-vis in CH3CN: λmax in nm (εmax, M⁻¹·cm⁻¹): ~660 (sh), 837 (397, br). ΛM (CH3CN) = 163 Ω⁻¹·cm²·mol⁻¹.
Synthesis of \([Cu(L)\)(NCS)]ClO_4\) (5): To a mixture containing Cu(ClO_4)_2·6H_2O (0.190 g, 0.50 mmol) and [bis(3,5-dimethyl-ethyl-pyrazol-1H-1-yl)-(3,4-dimethoxy-2-methylpyridyl)]amine, L^3 (0.206 g, 0.50 mmol) dissolved in MeOH (20 mL), NH_4NCS (0.038 g, 0.50 mmol) was added. The dark green solution was heated to boiling and filtered, while hot through celite. After 2 h, the resulting green precipitate, which separated was collected by filtration, washed with propan-2-ol, ether and dried in air (yield: 0.30 g, 95%). Recrystallization of the product from H_2O afforded medium spring green single crystals suitable for X-ray analysis. Characterization: Anal. Calcd. for C_{33}H_{34}ClCuN_{10}O_{4.67} (MM = 624.64 g/mol): C, 44.22; H, 5.54; N, 22.42%. Found: C, 44.42; H, 5.56; N, 22.48%. Selected IR bands (ATR, cm\(^{-1}\)):

- 3121 (w), 3089 (w), 2935 (w), 2844 (w) ν(C-H); 2091 (s) ν as(N≡O) (NCS\(^-\)); 1604 (m), 1552 (m), 1438 (m), 1309 (s), 1236 (w); 1073 (vs) ν(Cl-O) (ClO_4\(^-\)). UV-vis (CH_3CN): \(λ_{\text{max}}\) in nm (\(ε_{\text{max}}, M^{-1}cm^{-1}\)): 387 (1020), ~630 (sh), ~940 (76). \(Λ_{\text{M}}\) (CH_3CN) = 149 \(\Omega^{-1}\cdot cm^{2}\cdot mol^{-1}\).

Synthesis of \([Cu(tedmpza)(dca)]ClO_4·0.67H_2O\) (6): A mixture of Cu(ClO_4)_2·6H_2O (0.190 g, 0.50 mmol) and tris(3,5-dimethyl-1H-pyrazol-1-yl)ethylamine (tedmpza) dissolved in MeOH (20 mL) was treated with an aqueous solution containing Nadca (0.045 g, 0.50 mmol in 10 mL H_2O). This was followed by heating for 10 min, filtration through celite and the solution was allowed to stand at room temperature. The bluish green crystalline compound, which was isolated after four days (yield: 0.185 g, 60%) was recrystallized from CH_3OH to afford shiny bluish green single crystals suitable for X-ray analysis. Characterization: Anal. Calcd. for C_{34}H_{34}ClCuN_{10}O_{4.7} (MM = 623.61 g/mol): C, 43.60; H, 5.09; N, 15.47%. Found: C, 43.81; H, 5.06; N, 15.65%. Selected IR bands (ATR, cm\(^{-1}\)):

- 3435 (s,b), 3405 (s), 3385 (s), 3357 (s), 3284 (s), 3252 (s), 3186 (s), 3159 (s), 3126 (s), 3076 (w), 2946 (w), 2848 (w) ν(C-H); 2770 (w), 2694 (w), 2467 (w), 2300 (m), 2216 (s), 2176 (vs), 2137 (vs) ν as(N≡C) (dca); 1629 (w), 1552 (s), 1465 (m), 1424 (m), 1390 (m), 1331 (w) (pyrazolyl ring); 1091 (s) ν(Cl-O) (ClO_4\(^-\)). UV-vis in CH_3CN: \(λ_{\text{max}}\) in nm (\(ε_{\text{max}}, M^{-1}cm^{-1}\)): 387 (1020), ~630 (s), ~940 (76). \(Λ_{\text{M}}\) (CH_3CN) = 147 \(\Omega^{-1}\cdot cm^{2}\cdot mol^{-1}\).

Synthesis of \([Cu(L^4)(dca)]ClO_4·2H_2O\) (7): This was synthesized as described above for 6 except [bis(2-methylpyridyl)-(3,4-dimethoxy-2-methylpyridyl)]amine, L^4 was used instead of tedmpza. The complex was isolated as bluish green crystalline compound after 2 days (overall yield: 0.220 g, 71%). Characterization: Anal. Calcd. for C_{35}H_{36}ClCuN_{10}O_{4.67} (MM = 615.48 g/mol): C, 42.93; H, 4.26; N, 15.93%. Found: C, 42.80; H, 4.14; N, 15.93%. Selected IR bands (ATR, cm\(^{-1}\)):

- 3430 (s), 3412 (s), 3385 (s), 3357 (s), 3284 (s), 3252 (s), 3186 (s), 3159 (s), 3126 (s), 3076 (w), 2946 (w), 2848 (w) ν(C-H); 2770 (w), 2694 (w), 2467 (w), 2300 (m), 2216 (s), 2176 (vs), 2137 (vs) ν as(N≡C) (dca); 1604 (m), 1552 (m), 1465 (m), 1424 (m), 1366 (m), 1308 (m); 1090 (vs), 1067 (vs) ν(Cl-O) (ClO_4\(^-\)); 843 (w), 769 (m), 625 (m). UV-vis in CH_3CN: \(λ_{\text{max}}\) in nm (\(ε_{\text{max}}, M^{-1}cm^{-1}\)): 350 (923), ~665 (sh), ~940 (110, br). \(Λ_{\text{M}}\) (CH_3CN) = 147 \(\Omega^{-1}\cdot cm^{2}\cdot mol^{-1}\).

3.3. X-ray Crystal Structure Analysis

Suitable single crystals of 1-6 were carefully selected under polarizing microscope and mounted on a goniometer head. A Bruker-AXS APEX II CCD diffractometer (Karlsruhe, Germany) operating with Mo-Kα radiation (\(λ = 0.71073\) Å) at 100(2) K was used for single crystal data collection. In Table 4 relevant crystallographic data together with some features of the structure refinements are summarized. APEX and the SADABS computer programs \([63–65]\) were used for data processing, LP and absorption corrections. The SHELX \([66,67]\) program library was used for structure solution (direct methods) and refinement (full-matrix least-squares methods with F^2 data). Non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms were located from difference Fourier maps, and included in the refinements with isotropic displacement factors. HFIX geometrical constraints were applied for H atoms with parent C atoms. Additional computer programs: Mercury and PLATON \([68,69]\).
Table 4. Crystallographic data and processing parameters of 1–6.

| Compound | 1          | 2          | 3          |
|----------|------------|------------|------------|
| **Empirical formula** | C18H21CuN5O2S2 | C16H23CuN5OS2 | C15H16ClCuN7O4 |
| **Formula mass** | 467.01 | 465.09 | 477.51 |
| **System** | Monoclinic | Monoclinic | Orthorhombic |
| **Space group** | P21/c | P21/c | P212121 |
| **a (Å)** | 9.9325(18) | 8.037(3) | 8.2797(3) |
| **b (Å)** | 7.6958(14) | 28.198(9) | 10.3404(4) |
| **c (Å)** | 26.491(5) | 9.219(3) | 25.1838(10) |
| **α (°)** | 90 | 90 | 90 |
| **β (°)** | 95.923(3) | 93.416(5) | 90 |
| **γ (°)** | 90 | 90 | 90 |
| **V (Å³)** | 2014.8(6) | 2085.6(12) | 2156.12(14) |
| **Z** | 4 | 4 | 4 |
| **T (K)** | 100(2) | 100(2) | 100(2) |
| **µ (mm⁻¹)** | 1.316 | 1.267 | 1.173 |
| **Dcalc (Mg/m³)** | 1.540 | 1.481 | 1.471 |
| **θ max (°)** | 26.349 | 26.395 | 24.999 |
| **Data collected** | 14,125 | 12,796 | 71,092 |
| **Unique refl./Rint** | 4099/0.0268 | 4193/0.1191 | 3756/0.0437 |
| **Parameters/Restraints** | 256/0 | 257/0 | 260/0 |
| **Goodness-of-Fit on F²** | 1.074 | 1.123 | 1.110 |
| **R1/wR2 (all data)** | 0.0373 | 0.0943 | 0.0152 |
| **Residual extrema (e/Å³)** | 1.119/−0.465 | 1.215/−0.998 | 0.210/−0.150 |

The structure 3 crystallizes in chiral space group P212121 includes only a single ligand enantiomer (R at each chiral N) and Flack parameter is 0.022(8). In structure of 5 a void centered at position 0.393, 0.568, 0.914 is separated by 3.22 Å from O2 acceptor atom. Its size of 37 Å³ corresponds to volume of one water molecule. No SQUEEZE treatment was applied. In case of 4 low but still acceptable crystal quality causes Rint of 0.141 and poor data/parameter ratio of 9.94.
4. Conclusions

Two series of geometrical five-coordinated pseudohalido-Cu(II) complexes were separated and structurally characterized: distorted square pyramidal: \([\text{Cu}(\text{L}^1)(\text{NCS})_2]\) (1), \([\text{Cu}(\text{L}^2)(\text{NCS})_2]\) (2), and \([\text{Cu}(\text{L}^3)(\text{NCS})\text{ClO}_4]\) (5), and distorted trigonal bipyramidal: \([\text{Cu} (\text{isp}_3\text{tren})(\text{N}_2)]\text{ClO}_4\) (3), \([\text{Cu} (\text{isp}_3\text{tren})(\text{dca})]\text{ClO}_4\) (4), and \([\text{Cu} (\text{tedmpza})(\text{dca})]\text{ClO}_4\cdot0.67\text{H}_2\text{O}\) (6). The geometrical identities of the complexes were also determined in solution and results are compared to other related reported compounds as well as to those derived from halido-Cu complexes with similar stereochemistry. In the pseudohalido complexes the consistency between the molecular and the assigned structures in solution was excellent (Tables 1 and 2) indicating we can rely with confidence that the molecular geometrical structure, which was determined in the solid state is retained in solution. On the other hand, in the five-coordinated halido-Cu(II) complexes the picture was a little bit complicated as it was turned out that the molecular structure geometries, sometimes do not persist in solutions and may stereochimically change and/or hydrolyzed as this was observed in \([\text{Cu} (\text{6-MeTPA})\text{C}]^+\) (Table 3: 42, 43) and \([\text{Cu} (\text{BPA})\text{A})\text{Cl}]^+\) (51 and 52) [8,55] and in the dist. SP series \([\text{Cu}(\text{L}^3)\text{Cl}_2]\) (61), \([\text{Cu}(\text{L}^{10})(\text{H}_2\text{O})\text{Cl}_2]\) (62), and \([\text{Cu}(\text{L}^{11})(\text{Br}_2)]\) (63) [49–51]. This result is important because five-coordinated halido-Cu(II) complexes, which are constructed from N-donor coligands are widely used as potential anticancer agents and to mimic biological systems [3–8,44,49–52] and under these conditions the geometry and possibly the identity of the reactive species could be different from the originally isolated solid [5–8,44,49–52]. In these cases, results in solutions must be handled with great care and we cannot rely with confidence on molecular structure determination to assign the structures in solutions.

To account for why a sterースpecific geometry is adopted by a given five-coordinated Cu(II) compound (TBP vs. SP), number of parameters including chelate ring size, nature and steric environment imposed in the coligand’s skeleton were addressed [22–24]. In general, TBP structures are dominating in the solid state when the central Cu²⁺ ion is coordinated to tripod tetradeutate ligands containing only five-membered chelate rings (Tables 1 and 3: 3, 4, 20–22, 36, 37, 39–41, 54, 56–60) [8,27–29,41,52–54]. Also, the tendency for stabilization of SP geometry is enhanced (18, 30–32, 47–50) [23,30,43,48,56,57] as the chelate ring sizes are increased to six-membered through insertion of CH₂ group(s) into the ethylenic tripod arms. Interestingly, this analysis was proved to be universal in other five-coordinated complex ions such \([\text{Cu}(\text{tren})(\text{NH}_3)]^{2+}\), \([\text{Cu}(\text{Me}_3\text{tren})(\text{NCCH}_3)]^{2+}\), \([\text{Cu}(\text{TPA})(\text{H}_2\text{O})]^2+\) and \([\text{Cu}(\text{233})(\text{NH}_3)]^{2+}\) \((233 = N-(2\text{-aminoethyl})-N,N\text{-bis}(3\text{-aminopropyl})\text{amine})\), where the first three complexes were displaying distorted TBP geometry, whereas the latter one exhibits distorted SP geometry [55,70–72]. The tendency for SP structures was also observed when CH₃ groups were introduced at the 6th positions of the pyridyl arms in TPA or when one of the pyridyl groups was replaced with quinolyl groups [42, 43, 45, 52] [8,56]. Distorted SP environment was clearly dominating in all complexes derived from tetradeutate ligands regardless the chelate ring sizes (1, 2, 8–16, 30) [22–24,40,42,43], the macrocyclic complex \([\text{Cu}(\text{cyclen}\cdot\text{tpam})(\text{NCS})]\text{ClO}_4\cdot3\text{H}_2\text{O}\) (19) [23] as well as in \([\text{Cu}(\text{Medpt})(\text{ONO})(\text{H}_2\text{O})]^+\) \((\tau = 0.03)\) and \([\text{Cu}(\text{dien})(\text{ONOO})]^+\) \((\tau = 0.13)\), where Medpt = 3,3’-diamino-N-methylidipropylamine and dien = diethylentriamine [73]. However, still some few contradictions exist in the geometrical behaviors of the SP \([\text{Cu}(\text{tedmpza})(\text{N}_2)]\text{ClO}_4\) (31) [23] and its corresponding distorted TBP structure \([\text{Cu}(\text{tedmpza})(\text{dca})]\text{ClO}_4\cdot0.67\text{H}_2\text{O}\) (6), which was expected to display SP geometry based on the previous analysis as well as in \([\text{Cu}(\text{tepza})(\text{NCS})]\text{ClO}_4\) (17), which exhibits intermediate geometry and the TBP \([\text{Cu}(\text{tepza})(\text{dca})]\text{ClO}_4\) (38) [25], where both were predicted to display distorted SP geometry.

Supplementary Materials: The following are available online. CCDC 2008941-2008946 contains the supplementary crystallographic data for 1–6, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Selected bond lengths (Å) and angles (°) for the compounds under investigation are given in Tables S1–S3 and their corresponding packing views are shown in Figures S1–S6 for 1–6 coordination compounds, respectively. Coordination figures of Cu₁ and Cu₃ of 6 are given in Figures S7 and S8, respectively. The UV-vis spectra of the seven complexes under investigation are given in Figures S9–S15. Possible hydrogen bonds for compounds 1–6 are shown in Table S4.
Author Contributions: F.A.M., R.C.F., and A.T. performed the X-ray structural analysis. S.S.M., M.M.H., F.R.L., and N.M.H.S. contributed in the synthesis and spectral characterization of the designed compounds. F.A.M., S.S.M., F.R.L., and N.M.H.S. contributed to the writing of the manuscript. All authors have read and agreed to the published version of the manuscript.

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**Sample Availability:** Not available.

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