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Variable Unidentate Ligands in Cu(I)(XXY) and Cu(I)(XYZ) Complexes—Structural Aspects

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Abstract: This manuscript provides a structural analysis of over eighty copper(I) compounds mostly reported in the Cambridge Structural Database (CSD) version 5.45 in which unidentate ligands build up various inner coordinate spheres. These complexes crystallized in four crystal classes: trigonal (1 example), triclinic (10 examples), orthorhombic (13 examples), and monoclinic (58 examples). The analyzed complexes can be divided into two groups according to the type of coordinating ligands (L = X, Y, Z) incorporated into their structure: Cu(XXY) (more common) and Cu(XYZ). The structural data of L-Cu-L bond angles show that the angular distortion from the regular trigonal geometry grows with total mean values of deviation from 120.0°, in the order within the first group: 3.2°(Cu(IIP)) < 6.1°(Cu(ClClY)) < 6.5°(Cu(SSY)) < 8.2°(Cu(PPY)) < 8.9°(Cu(BrBrY)) < 16.9°(Cu(NNY)) < 19.8°(Cu(CCY)) < 25.5°(Cu(SeSeY)) and within the second group: 3.1°(Cu(SIP)) < 14.3°(Cu(SClP) < 15.5°(Cu(SBrP). The donor atoms are responsible for the distortion as follows: the soft donor atoms diminish the distortion while the borderline and the hard growing amplify the distortion. Given the importance of Cu(I) compounds in (bio)inorganic functional materials and catalysis, the correct interpretation of the geometry of Cu(I) complexes in terms of the coordination polyhedra is crucial for understanding the properties of the respective compounds.

Keywords: Cu(I)(XXY); Cu(I)(XYZ); complexes; unidentate ligands; structural analysis; distortion

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1. Introduction

Stereospecificity in coordination compounds is usually linked to crucial stereospecificity in biological systems, catalysis, and stereochemical effects in industrial processes. Structural parameters of metal complexes, resulting in their stereospecificity, are affected by many parameters, such as the oxidation state of the metal, coordination number, character of donor and acceptor atoms integrated into the complex structure, etc.

For the spherically symmetric d10 Cu(I) ion, common coordination geometries include two-coordinate linear, three-coordinate trigonal planar, and four-coordinate tetrahedral arrangements [1,2].

Copper compound chemistry has been extensively explored, focusing on the relationship between structure and reactivity, which holds significant importance in areas such as industrial catalysis and biomedical activity [3–8]. Although copper(I) is highly susceptible

to oxidation in air and is not stable in aqueous solutions, many stable compounds have been synthesized using ligands with soft pi-acid properties. Additionally, some copper(I) complexes remain relatively stable due to their extremely low solubility. Phosphine ligands are among the most effective in stabilizing copper(I) coordination compounds [9]. Boron cluster anions (primarily the closo-decaborate anion) and carboranes are also capable of stabilizing copper(I) in reaction solutions even in the presence of other ligands, forming a great number of homoleptic and heteroleptic copper(I) complexes [10,11].

Recently, photocatalyzed and photosensitizer chemical processes have gained increasing interest, becoming some of the most active fields in chemical research. This surge in interest is driven by their applications in diverse fields such as medicine, chemical synthesis, materials science, and environmental chemistry. Within all homogeneous catalytic systems, photoactive copper(I) complexes are especially attractive [12,13]. Electrolytic copper complexes show significant promise for noble metal-free photocatalysis and even photochemistry. The $[Cu(N^{\wedge}N)(P^{\wedge}P)]^{+}$ complexes activity is particularly important in photocatalyzed transformations, especially for proton and CO_2 reduction, as well as in other photochemical applications like sensors [12]. Copper(I) complexes are considered promising low cost, abundantly available alternatives for photosensitizers in solar energy conversion technologies [13]. They have been applied in dye-sensitized cells as redox mediators and additionally as dyes [14]. Neutral copper(I) complexes, known for their high emission quantum efficiency and rapid photoluminescence response time, are considered promising materials for organic light-emitting diodes (OLEDs). Specifically, Cu(I) complexes exhibiting thermally activated delayed fluorescence (TADF) are among the most potential candidates for lighting devices of next generation [15]. Several Cu(I) complexes have been synthesized and evaluated in vitro as potential anti-cancer agents. Copper(I) complexes of thiosemicarbazones and their derivatives have demonstrated significant potential in cancer chemotherapy [16]. Additionally, mixed-ligand Cu(I) complexes incorporating triazolyl borate and alkyl- or aryl-phosphines have shown effectiveness against A549 adenocarcinoma cells, which are resistant to the commonly used anticancer drug cisplatin [17].

The above-mentioned examples of areas of practical use of Cu(I) complexes highlight the necessity of their detailed structural analysis to elucidate the importance and relationship between particular structural parameters affecting stereospecificity and, by that, properties of Cu(I) complexes. Recently, we have provided a series of structural studies focused on systematic structural analysis of Cu(I) complexes. In the first study, we analyzed the structural data of linear X-Cu-X complexes [18]. The second study was devoted to the analysis of the structural data of bent X-Cu-Y complexes. X-Cu-Y complexes with variable combinations of donor atoms were divided into organo-metallics, such as C-Cu-Y (Y = HL, OL, NL, SL, SiL, PL, Cl, Br, I, AlL, or SnL) and coordination complexes, such as N-Cu-Y (Y = OL, Cl, S-Cu-Y, Cl, Br, I), P-Cu = Y, (Y = Cl, I), and Se-Cu-Y, (Y = Br, I) [19]. In the third study, the structural data of homo-Cu(XXX) where each X represents an unidentate ligand, namely X_3 = N_3, C_3, Cl_3, S_3, P_3, Br_3, were analyzed [20]. There was a wide variability of unidentate ligands involved in these studies enabling us to analyze the effect of their structural characteristics, e.g., type of donor atom, on the distortion of complexes within the particular coordination groups, do mutual comparisons, and reveal trends.

Analogically, as a logical continuation of our latest published work [20] on the structural analysis of Cu(XXX) complexes with three unidentate ligands X, this study is devoted to Cu(XXY) and Cu(XYZ) complexes. The following structural subgroups of the Cu(I) complexes were identified, analyzed, and discussed: Cu (NNY) (Y = O, C, Cl, S, Br, I); Cu (CCY) (Y = O, Cl, P, Br, I); Cu (SSY) (Y = N, Cl, I); Cu(SeSeY); (Y = Cl, Br, I); Cu(PPY)

(Y = O, C, Cl, Br, I); Cu(ClClY) (Y = NP); Cu(BrBrY) (Y = N, P); Cu(IIP); Cu(SClP); Cu(SBrP); Cu(SIP).

2. Results and Discussion

There are 82 structures of copper(I) complexes in which the angular distortion from regular trigonal geometry occurs in Cu(XXY) and Cu(XYZ). In the former, a pair of monodentate ligands (XX) with different monodentate (Y) ligands create Cu(XXY) composition. In the latter, three different monodentate ligands build up Cu(XYZ) derivatives where X = S and Z = P, i.e., Cu(SYP) composition.

2.1. Cu(NNY) (Y = O, C, Cl, S, Br, and I); Cu(CCY) (Y = O, Cl, P, Br, and I) Derivatives

The copper(I) complexes of the Cu(NNY) type by far prevail, not only by many examples but also by the variations of Y ligands. In orthorhombic $[Cu(C_2H_3N)_2(C_{27}H_{36}N_2)]SbF_6C_7H_8$ [21], monoclinic $[Cu(py)_2(C_{27}H_{36}N_2)]BF_4$ [21], monoclinic $[Cu(C_{11}H_9N)_2(C_{27}H_{36}N_2)]BF_4$ [22], and orthostates $[Cu(2\text{-}Mepy)_2(C_{27}H_{36}N_2)]BF_4$ [21]. The total mean values of Cu-L bond distances are 2.026 (±12) Å (L = N) and 1.895 (±5) Å (L = C). The total mean values of N-Cu-N bond angles are 99.0 (±6)° and N-Cu-C are 126.6 (±1.2) and 134.4 (±2.6)°, respectively.

In four copper(I) complexes, pair of monodentate N-donor ligands with chlorine build up an angular distortion, such complexes are monoclinic $[Cu(2\text{-}Mepy)_2Cl]$ [22], monoclinic $[Cu(2,6\text{-}Me_2py)_2Cl]$, and [22] orthorhombic $[Cu(C_6H_{12}N_2)_2Cl]$ [23]. As an example, the structure of $[Cu(C_6H_{12}N_4)_2Cl]$ [23] is illustrated in Figure 1.

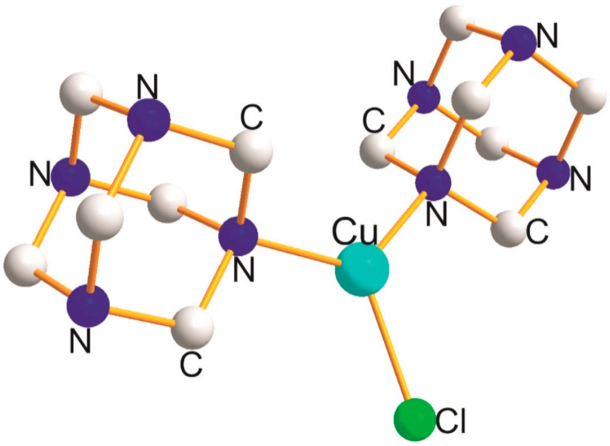

Figure 1. Structure of $[Cu(C_6H_{12}N_2)_2Cl]$ [23].

The orthorhombic $[Cu(C_5H_6N_2)_2Cl][Cu(C_5H_6N_2)_2]Cl$ [24] contains two Cu(I) atoms, one with the inner coordination sphere Cu(NNCl), and the second has Cu(NN). Monoclinic $[Cu(C_5H_6N_2)_2Cl][Cu(C_5H_6N_2)_2(ONO_2)]$ [25] also contains two Cu(I) atoms. Both are three coordinates of the Cu(NNCl) and Cu(NNO) types. The mean values of Cu-L bond distances for three coordinate complexes are 1.992 (±5) Å (L = N), 2.290 (±4) Å (L = Cl) and 1.935 Å (L = O). The mean values of L-Cu-L bond angles are 138.6 (±11.0)°(N-Cu-N), 106.0 (±9.5)°(N-Cu-Cl), and 112.0°(N-Cu-O).

Triclinic $[Cu(C_2H_3N)_2(C_{64}H_{78}N_6PS)](PF_6)_2(CH_3CN)_2$ [26] is the only example of Cu (NNS) type. The Cu-L bond distances are 1.995 (L = N) and 2.322 Å (L = S). The values of respective angles are 127.0°(N-Cu-N) and 108.0 (±4)°(N-Cu-S).

In another four copper(I) complexes: monoclinic $[Cu(2,6\text{-}Me_2py)_2Br]$ [26], monoclinic $[Cu(PhMe_2pz)_2Br]$ [27], triclinic $[Cu(3,5\text{-}Me_2py)(2,4,6\text{-}Me_3py)Br]$ [28], and orthorhombic $[Cu(C_6H_{12}N_4)_2Br]$ [23], a pair of monodentate N-donor ligands with bromide build up angular distortion (Cu(NNBr)) type.

The mean values of Cu-L bond distances are 1.985 (±25) Å (L = N) and 2.402 (±39) Å (L = Br). The mean values of L-Cu-L bond angles are: 133.8 (±9.1)°(N-Cu-N) and 113.1 (±4.5)°(N-Cu-Br).

There are three monoclinic complexes: α-[Cu(2,6-Me_2py)$_2$I] [29], β-[Cu(2,6-Me_2py)$_2$I] [29], [Cu(bpbim)$_2$I]thf [30] and two orthorhombic [Cu(2-Mequ)$_2$I] [28] and [Cu($C_{12}H_{11}N_2$)I] [31] in which monodentate N-donor ligands with iodo form angular distortion, Cu(NNI). The mean values of Cu-L bond distances are 1.992 (±22) Å (L = N) and 2.602 (±85) Å (L = I). The mean values of N-Cu-N and N-Cu-I bond angles are 135.4 (±14.1)° and 113.5 (±7.8)°, respectively.

The total mean values of Cu-L bond distances elongate with covalent radius of donor atom in the following order: 1.895 (±5) Å (L = C, 0.77Å) < 2.290 (±4) Å (L = Cl, 0.99°) < 2.322 Å (L = S, 1.02 Å) < 2.402 (±6) Å (L = Br, 1.14 Å) < 2.602 (±85)Å (L = I, 1.33Å).

The degree of angular distortion from regular trigonal geometry depends on the values of the respective L-Cu-L angles.

For the perfect trigonal geometry, the values are 120°. Any deviation from the values reflects the degree of distortion. The degree of distortion for Cu(NNY) complexes increases in the order of the total mean values of the respective L-Cu-L angles, and these are 130.5°(N-Cu-N), 108.0 (±2.3)°(N-Cu-S) < 133.8 (±9.1)°(N-Cu-N), 113.1 (±4.5)°(N-Cu-Br) < 135.4 (±4.5)°(N-Cu-N), 113.5 (±7.6°) (N-Cu-I) < 136.6 (11.0)°(N-Cu-N), 106.6 (±9.5)°(N-Cu-Cl) < 99.0 (±6) (N-Cu-N), and 130.5 (±4)°(N-Cu-C).

There are complexes where monoclinic [Cu(p-tol NC)$_2$(2.6-$Bu^t{}_2C_6H_3O$)] [32], orthorhombic [Cu($C_{11}H_{22}N_4$)$_2$Cl] [33], orthorhombic [Cu($C_{11}H_{22}N_4$)$_2$Br] [34], orthorhombic [Cu($C_{20}H_{16}N_4$)$_2$Cl] [34], triclinic [Cu($C_{20}H_{16}N_4$)$_2$Br] [34], triclinic [Cu($C_{13}H_{18}N_2$)$_2${(Me_3Si)$_2$P}] [35] (Figure 2), and monoclinic [Cu($C_{20}H_{16}N_4$)$_2$I]2(thf) [34] in which monodentate ligands build up angular distortion from regular trigonal geometry of the types Cu (CCY) (Y = O) [32]; Cl [33,34]; Br [33,34]; P [35]; I [34]. The total mean value of Cu-L bond distance is 1.923 (±23) Å. The values of Cu-Y bond distances elongate with covalent radius of donor atoms in the sequence: 1.917 Å (Y = O, 0.73 Å) < 2.336 Å (Cl, 0.99 Å) < 2.377 Å (P, 1.06 Å) < 2.432 Å (Br, 1.14 Å) < 2.515 Å (I, 1.33 Å). The degree of distortion increases with the deviation of the respective angles from 120°, in the order: 121.5°(C-Cu-C), 118.6 (±3.2)–Cu-O) < 129.5°(C-Cu-C), 115.8 (±2.8)°(C-Cu-Cl) < 130.2°(C-Cu-C), 114.8 (±2.6)°(C-Cu-P) < 132.7°(C-Cu-C), 113.6 (±1.8)°(C-Cu-Br) < 135.4°(C-Cu-C), and 112.4 (±3.5)°(C-Cu-I).

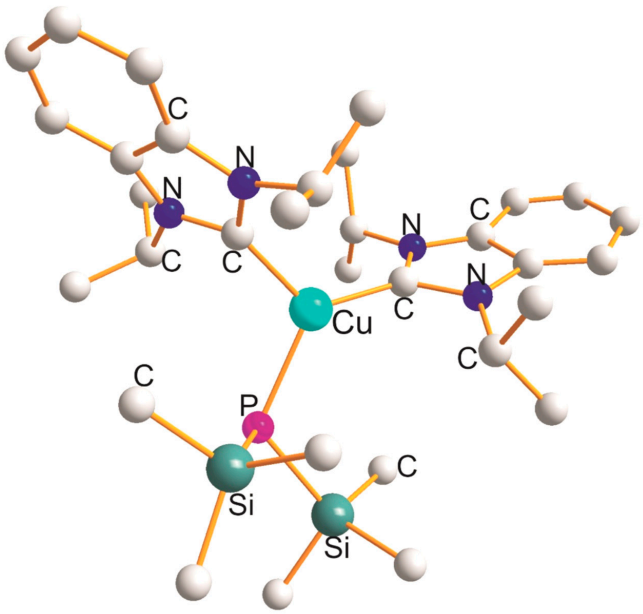

Figure 2. Structure of [Cu($C_{13}H_{18}N_4$)$_2${(Me_3Si)$_2$P}] [35].

2.2. Cu(SSY), (Y = N, Cl, I), Cu(SeSeY) (Y = Cl, Br, I) Derivatives

Much attention was paid to monodentate ligands which create Cu(SSY) (Y = N, Cl, I) types, especially with Y = Cl. In monoclinic $[Cu(imt)_2(SCN)]$ [36], the ligands build up Cu(SSN) type. The Cu-L bond distances are 2.221 Å (L = S, mean) and 1.956 Å (L = N). The values of the respective angles are 121.6°(S-Cu-S) and 119.2°(S-Cu-N).

There are copper(I) complexes in which unidentate ligands create Cu(SSCl) type. Such complexes are monoclinic $[Cu(tuc)_2Cl]$dmf [37], monoclinic $[Cu(Me_2imt)_2Cl]$ [37], monoclinic $[Cu(Hmpt)_2Cl]$ [38], monoclinic $[Cu(C_{12}H_{11}N_3S)_2Cl]$ [39], monoclinic $[Cu(C_3H_4N_2S_2)_2Cl]$ [40], monoclinic $[Cu(C_4H_8N_2S)_2Cl]$ [41], monoclinic $[Cu(C_6H_{12}N_2S)_2Cl]$ [41], monoclinic $[Cu(C_9H_{14}N_2O_2S)_2Cl]$ [42], orthorhombic $[Cu(C_{10}H_{12}N_2O_3S)_2Cl]$ [43], monoclinic $[Cu(C_{13}H_{14}N_2O_2S)_2Cl]$ [44], monoclinic $[Cu(C_{16}H_{18}N_2O_2S)_2Cl]$ [45], and triclinic $[Cu(C_{17}H_{20}N_2S)_2Cl]$thf [46].

The total mean values of Cu = L bond distances are 2.225 (±8) Å (L = S) and 2.250 (±20) Å (L = Cl).

In another three complexes, monoclinic $[Cu(tclH)_2I]$ [47], monoclinic $[Cu(C_{23}H_{30}N_2OS)_2I]$ [48] (Figure 3), and orthorhombic $[Cu(C_9H_{21}PS)_2I]$ [48], monodentate ligands forms Cu(SSI) type. The total mean values of Cu-L bond distances are: 2.239 (±5) Å (L = S) and 2.534 (±56) Å (L = I). The total mean values of the respective angles are: 112.6 (±8.4)°(S-Cu-S) and 124.5 (±3.7)°(S-Cu-I).

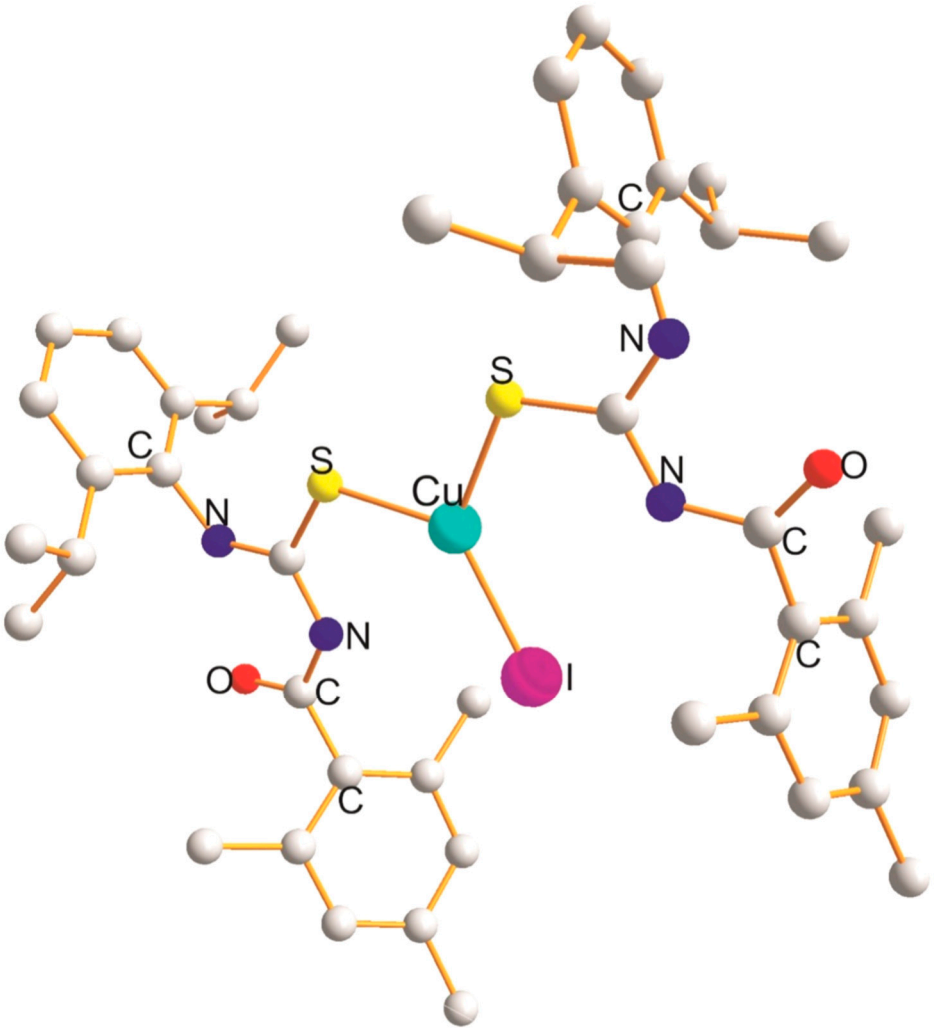

Figure 3. Structure of $[Cu(C_{23}H_{30}N_2OS)_2I]$ [48].

The degree of distortion increases in the order: 119.9 (±41)°(S-Cu-S), 119.1 (±5)°(S-Cu-Cl) < 121.6°(S-Cu-S), 119.2 (±3)°(S-Cu-N) < 121.1 (±2)°(S-Cu-S), and 124.5 (±2.7)°(S-Cu-I).

In copper(I) complexes, orthorhombic [$Cu(C_9H_{21}PSe)_2Cl$] [48], orthorhombic [$Cu(C_9H_{21}PSe)_2Br$] [48], and orthorhombic [$Cu(C_9H_{21}PSe)I$] [48], the unidentate ligands induce an angular distortion from the ideal trigonal geometry. The mean values of Cu-L bond distance elongate with a covalent radius of coordinate atom in the sequence: 2.214 Å (Cl, 0.99 Å) < 2.349 Å (Br, 1.14 Å) < 2.397 (Se, 1.17 Å) < 2.588 Å (I, 1.33 Å). The values of the respective angles are 104.3°(Se-Cu-Se), 129.4 (±21)°(Se-Cu-Cl), 101.1°(Se-Cu-Se), 129.4 (±3.0)°(Se-Cu-Br), 103.7°(Se-Cu-Se), and 127.6 (Se-Cu-I).

2.3. Cu(PPY) (Y = O, C, Cl, Br, and I) Derivatives

Twelve complexes, in addition to a pair of unidentate P-donor ligands with Y-ligands, exhibit angular distortion from the ideal trigonal geometry. The Cu(PPO) type is in monoclinic [$Cu(Pcy_3)_2(OClO_3)$] [49], triclinic [$Cu(PPh_3)_2(C_3H_3O_4)]CH_2Cl_2$ [50], monoclinic [$Cu(PPh_3)_2(C_4H_5O_4)$] [51], monoclinic [$CuPcy_3)_2(C_3H_2NO_2)$] [51], and monoclinic [$Cu(PPh_3)_2(C_7H_9N_2O_6)$] [52]. The total mean values of Cu-L bond distances are 2.117 (±8) Å (L = O) and 2.250 (±10) Å (L = P). The values of L-Cu-L bond angles are 134.9 (±9.0)°(P-Cu-P) and 112.1 (±4.5)°(P-Cu-O).

The Cu(PPC) type was formed only in monoclinic [$Cu(PPh_3)_2\{(CF_3)_2FC)\}$] (Figure 4) [53]. The Cu-L bond distances are 2.002 Å (L = C) and 2.265 (±11) Å (L = P). The values of the respective angles are 114.1°(P-Cu-P) and 122.9 (±4.5)°(P-Cu-C).

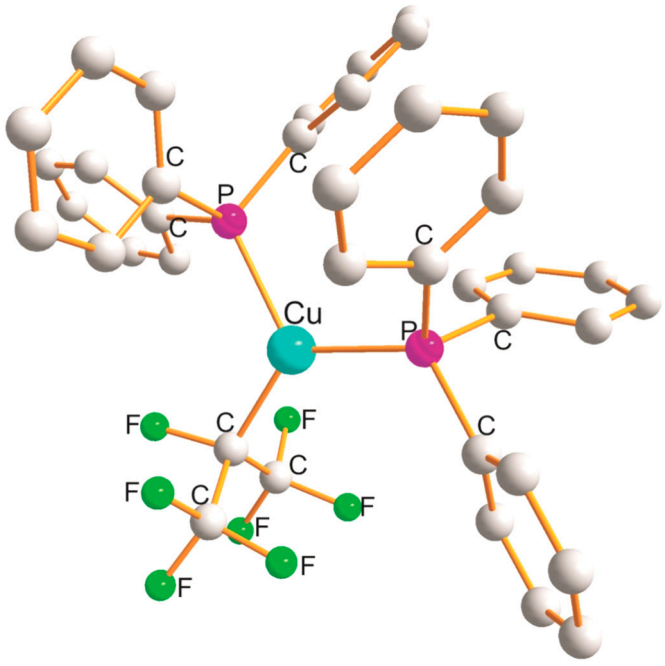

Figure 4. Structure of [$Cu(PPh_3)_2\{(CF_3)_2FC\}$] [53].

Another six complexes are of Cu(PPCl) type. Such complexes are orthorhombic [$Cu(Pcy_3)_2Cl$] [54], monoclinic [$Cu(C_{18}H_{14}P)_2Cl]0.5(CH_3CN)$ [55], monoclinic [$Cu(C_{22}H_{19}S_2P)_2Cl$] [56], monoclinic [$Cu(C_{15}H_{21}BNP)_2Cl$] [57], triclinic [$Cu(PPh_3)_2Cl]0.5(C_6H_6)$ [58], and monoclinic [$Cu\{PPh_2(2\text{-}MePh)\}_2Cl$] [59].

The total mean values of Cu-L and L-Cu-L bond angles are 2.228 (±23) Å (L = Cl), 2.254 (±12) Å (L = P), 131.0 (±9.0)°(P-Cu-P), and 117.5 (±2.6)°(P-Cu-Cl).

There are three complexes; monoclinic [$Cu(C_{15}H_{21}BNP)_2Br$] [57], monoclinic [$Cu\{PPh_2(2\text{-}OHCPh\}_2Br$] [59], and triclinic [$Cu(PPh_3)_2Br]0.5(C_6H_{6)}$ [60] in which unidentate ligands build up a trigonal geometry of a Cu(PPBr) type. The total mean values of (Cu-L and

L-Cu-L) are 2.257 (±1.8) Å (L = P), 2.363 (±43) Å (L = Br), 125.6 (±1.8)°(P-Cu-P), and 116.9 (±2.8)°(P-Cu-Br).

In four monoclinic complexes, [(Cu($C_{15}H_{21}BNP)_2$I] [57], [Cu($PPh_3)_2$I] [59], [Cu{PPh_2(2-OHCPh)}$_2$I] [59], and [Cu($C_{19}H_{15}OP)_2$I] [61], unidentate ligands build up trigonal geometry of Cu(PPI) type. The total mean values of (Cu-L) and (L-Cu-L) are 2.261 (±12) Å (L = P), 2.515 (±9) Å (L = I), 125.6 (±1.4)°(P-Cu-P), and 116.7 (±8)°(P-Cu-I).

2.4. Cu(ClClY), Cu(BrBrY) (Y = N,P), and Cu(IIP) Derivatives

X-ray data reveal that angular distortion from the ideal trigonal geometry is present in the triclinic [Cu$(Cl)_2$(thm)] [62], which belongs to the Cu(ClClN) type. The values of Cu-L bond distances and L-Cu-L bond angles are 1.993 Å (L = N), 2.268 (±7) Å (L = Cl), 116.9°(Cl-Cu-Cl), and 121.5 (±14.5)°(Cl-Cu-N).

Data of monoclinic (NEt_4)[Cu$(Cl)_2$(PPh_3)] [58] and triclinic [Cu$(Cl)_2$($C_{34}N_{40}N_4P$)]2(CH_3CN) [63] occurs at Cu(ClClP) type. The mean values of data are 2.238 (±6) Å (L = Cl), 2.218 (±7) Å (L = P), 117.3 (±5) (Cl-Cu-Cl), and 122.6 (±1.0)°(Cl-Cu-P).

Triclinic [Cu$(Br)_2$(thm)] [64] is the only example of Cu(BrBrN) type. The structural data are 2.003 Å (L = N), 2.377 (±5) Å (L = Br), 115.3°(Br-Cu-Br), and 122.8 (±12.8)°(Br-Cu-N).

In four complexes, monoclinic (NPr_4)[Cu$(Br)_2$(PPh_3)] [59], orthorhombic (NBu_4)[Cu$(Br)_2$(PPh_3)] [58], monoclinic (PPh_3Me)[Cu$(Br)_2$(PPh_3)] [58], and monoclinic [Cu$(Br)_2$($C_{32}H_{53}NP$)] [65], unidentate ligands build up trigonal geometry of Cu(BrBrP) type.

The total mean values of Cu-L bond distances are: 2.369 (±8) Å (L = Br) and 2.221 (±11) Å (L = P). The total values of L-Cu-L bond angles are 115.9 (±8)°(Br-Cu-Br) and 122.0 (±6)°(Br-Cu-P).

Monoclinic (NBr_4)[Cu$(I)_2$(PPh_3)] [58] is only an example of Cu(IIP) type. The structural data are 2.528 (±13) Å (L = I), 2.225 Å (L = P), 118.6°(I-Cu-I), and 120.9 (±2.3)°(I-Cu-P).

2.5. Cu(SClP), Cu(SBrP), and Cu(SIP) Derivatives

Certain complexes feature an inner coordination sphere surrounding Cu(I), constructed by three different donor ligands. In monoclinic [Cu($C_{12}H_{11}N_3S$)(Cl)(PPh_3)] [39] and in trigonal [Cu(P(o-tolyl)$_3$)(Cl)(pymtH)] [65], the trigonal geometry of Cu(SClP) type form. The mean values of Cu-L bond distances are 2.219 (±3) Å (L = S), 2.265 (±28) Å (L = Cl), and 2.224 (±17) Å (L = P). The mean values of the respective angles are 117.8 (±5.2)°(S-Cu-Cl), 114.2 (±6)°(Cl-Cu-P), and 126.9 (±4)°(S-Cu-P).

Three unidentate ligands of triclinic [Cu{P(o-tolyl)$_3$}(Br)($C_4H_6N_2S$)] [66] form a trigonal geometry of Cu(SBrP) type. The structural data are 2.290 Å (L = S), 2.413 Å (L = Br), and 2.256 Å (L = P). The values of the respective angles are 134.4°(S-Cu-Br), 116.9°(Br-Cu-P), and 125.8°(S-Cu-P).

An almost regular trigonal geometry of the Cu(SIP) type was built up by the unidentate ligands of monoclinic [Cu{P(o-tolyl)$_3$}(I)($C_4H_6N_2S$)] (Figure 5) [65]. The values of Cu-L bond distance are 2.254 Å (L = S), 2.563 Å (L = I) and 2.269 Å (L = P). The values of the respective angles are 119.4°(S-Cu-I), 118.2°(I-Cu-P), and 120.7°(S-Cu-P).

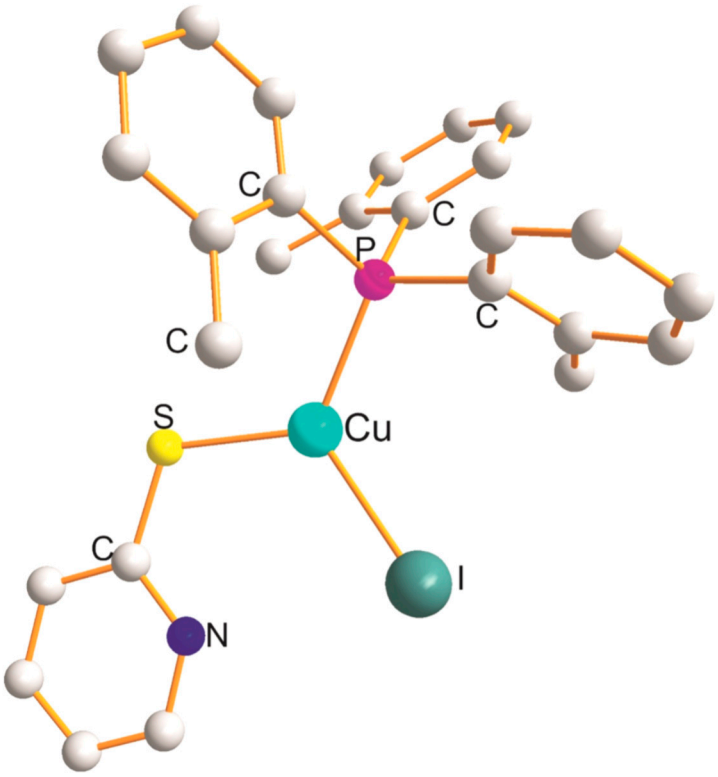

Figure 5. Structure of [Cu{(P(o-tolyl)$_3$(C_5H_4NS)I] [65].

3. Materials and Methods

In the structural study devoted to Cu(I) complexes, the Cambridge Crystallographic Database CSD version 5.45 (CCDC, Cambridge, UK) was used for the analysis of the structures. The program Diamond, Diamond Version 3.2k, serial no:1.3.2.20007208.2426 (Crystal Impact, Bonn, Germany) was used for creating the visualization of chemical structures. The complexes were selected for this analytical study according to well defined structural group characteristics, i.e., Cu(XXX) and Cu (XYZ) composition formulas, in which X, Y, and Z are unidentate ligands building up a tetrahedral geometry.

4. Conclusions

This manuscript has analyzed and classified 82 structures of coordinated copper(I) complexes, built up by unidentate ligands, containing structures that have been prepared by two methods. The initial method entails the reduction of a copper(II) salt in the presence of a ligand. These are primarily S and P donor molecules, acting as both ligands and reducing agents. The second, more prevalent approach involves the direct interaction of ligands with copper(I) salts in a non-aqueous solvent, such as acetonitrile, under an inert atmosphere (typically dry nitrogen).

These complexes crystallized in distinct four crystal classes: trigonal (1 example), triclinic (10 examples), orthorhombic (13 examples), and monoclinic (58 examples).

In the chemistry of "soft" copper(I), there was a wide variety of unidentate ligands forming an angular distortion from regular trigonal geometry. These complexes were divided into two groups. The first one of the Cu(XXY) and the second one of the Cu(XXY), and more specifically Cu(SXP) type.

The former is more common with the inner coordination spheres Cu(NNY), Cu(CCY), Cu(SSY), Cu(SeSeY), Cu(PPY), Cu(ClClY), Cu(BrBrY), and Cu(IIP). The unidentate Y is of a wide structural variety.

The total mean values of Cu-L bond distance elongate in the sequence 1.953 Å (L = C) < 1.986 Å (N) < 1.989 (O) < 2.223 Å (S) < 2.245 Å (P) < 2.259 Å (Cl) < 2.380 Å (Br) < 2.383 Å (Se) < 2.460 Å (I).

It is well known that the values of each of the three L-M-L angles for perfect trigonal geometry should each be 120°(3x). Hence, the distortion grows with a total mean deviation from the values of 120°in the order as summarized in Table 1.

Table 1. The total mean values of structural data (angles) for Cu(XXY) coordinated copper(I) compounds.

Cu(XXY)	(X-Cu-X)°	(X-Cu-Y)°$_2$	Σ (a + b)°
Cu(IIY)	I-Cu-I	(I-Cu-P)2	3.2
(Y = P)	118.6 (−1.4) [a]	120.9 (+1.8) [b]	
Cu(ClClY)	Cl-Cl-Cl	(Cl-Cu-Y)2	6.1
(Y = N, P)	117.9 (−2.1) [a]	122.0 (+4.0) [b]	
Cu(SSY)	S-Cu-S	(S-Cu-Y)2	6.5
(Y = N, Cl, I)	117.1 (−2.9) [a]	121.8 (+3.6) [b]	
Cu(PPY)	P-Cu-P	(P-Cu-Y)2	8.9
(Y = O, L, Cl, Br, I)	126.2 (+6.2) [b]	119.0 (−2.0) [a]	
Cu(BrBrY)	Br-Cu-Br	(Br-Cu-Y)2	8.2
(Y = N, P)	115.9 (−4.1) [a]	122.4 (+4.8) [b]	
Cu(NNY)	N-Cu-N	(N-Cu-Y)2	16.9
(Y = O, L, Cl, S, Br, I)	126.9 (+6.9) [b]	115.0 (−10) [a]	
Cu(CCY)	C-Cu-C	(C-Cu-Y)2	19.8
(Y = O, Cl, P, Br, I	129.8 (+9.8) [b]	115.0 (−10) [a]	
Cu(SeSeY)	Se-Cu-Se	(Se-Cu-Y)2	25.5
(Y = Cl, Br, I)	102.8 (−16.7) [a]	128.9 (+8.9) [b]	

[a] Values of the angles are lower than 120° (negative deviation); [b] values of the angles are higher than 120° (positive deviation); Σ (a + b)° = sum of the total mean deviations of the angles.

The data in Table 1 show that the angular distortion from regular trigonal geometry grows with deviation from 120° from the top to the bottom. It can be seen that a pair in Cu(IIY), Cu(SSY), Cu(PPY), and Cu(CCY) are "soft" atoms, Cu(BrBrI) are borderline, and the remaining Cu(ClClY) and Cu(NNY) are "hard". Also, Y-ligands are mostly "soft". There was no trend in rising distortion according to the softness or hardness of donor atoms detected from the analyzed dataset. On the other hand, particular trends in the subgroups of the soft, borderline, and hard donor atoms coordinating "soft" copper(I) were detected, as can be seen in Table 1.

The total mean values of Cu-L distance in the second group, i.e., in the Cu(XYZ) complexes, more specifically Cu(SClP), Cu(SBrP), and Cu(SIP), elongate in the sequence: 2.243 (±26) Å (L = P) < 2.246 (±22) Å (S) < 2.265 (±28) Å (Cl) < 2.413 Å (Br) < 2.463 Å (I). The mean values of the respective angles are shown in Table 2.

Table 2. The total mean values of structural data for Cu(XYZ) coordinated copper(I) compounds.

Cu(SIP)	Cu(SClP)°	Cu(SBrP)°
119.4 (−0.6)°(S-Cu-I)	117.8 (−2.2)°(S-Cu-Cl)	113.4 (−6.6) (S-Cu-Br)
118.2 (−1.8)°(I-Cu-P)	114.7 (−5.3)°(Cl-Cu-P)	116.9 (−3.1)°(Br-Cu-P)
120.7 (+0.7)°(S-Cu-P)	126.8 (+6.8)°(S-Cu-P)	125.8 (+5.8)°(S-Cu-P)
Σ3.1°	Σ14.3°	Σ15.5°

The data in Table 2 indicate that angular distortion from the ideal trigonal geometry increases from left to right. It can be seen that the character of donor atoms is responsible for the distortion. While the soft donor atoms diminish, the borderline and hard donor atoms grow distortion. The significance of such theoretical knowledge is clear in predicting

the structure–activity relationship when assuming an activity of a complex increases with the degree of distortion.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

$(Me_3Si)_2P$	(ditrimethylsilyl)phosphide
2,6-$Bu^t_2C_6H_3O$	2,6-di-t-butylhexadienal
2,6-Me_2py	2,6-dimethyl pyridine
2-Mepy	2-methyl pyridine
2-Mequ	2-methylimidazole
bpbim	1-benzyl-2-benzimidazole
$C_3H_2NO_2$	cyanoacetato
$C_3H_3O_4$	malonato
$C_3H_4N_2S_2$	5-methyl-1,3,4-thiadiazole-2(3H)-thione
$C_4H_5O_4$	succinato
$C_4H_8N_2S$	1-methylimidazolidine-2-thione
$C_5H_6N_2$	pyridin-4-amine
$C_6H_{12}N_2S$	1-propylimidazolidine
$C_6H_{12}N_4$	(1,3,5,7-tetra-azatricyclo[3.3.1.1^{3,7}]decane)
$C_7H_9N_2O_6$	3,5-dinitrobenzoato
$C_9H_{14}N_2O_2S$	ethyl-4,6-dimethyl-2-thioxo-1,2,3,4-tetra-hydropyrimidine-5-carboxylate
$C_9H_{21}PS$	tri-isopropylphosphine sulfide
$C_{10}H_{12}N_2O_3S$	methyl ((4-methoxyphenyl)carbonothioyl)carbamate)
$C_{11}H_{22}N_4$	2-t-butyl-5-(t-butylamino)-4-methyl-2,4-dihydro-3H-1,2,4-triazol-3-ylidene)
$C_{11}H_9N$	2- phenyl pyridine
$C_{12}H_{11}N$	3-methyl-2-phenylpyridine
$C_{13}H_{14}N_2O_2S$	(1-(2-methyl-4-(sulfanylidene)-3,4,5,6-tetrahydro-2H-2,6-methano-1,3,5-benzoxadiazocin-11-yl)ethan-1-one)
$C_{13}H_{18}N_2$	1,3-di-isopropylbenzimzadol-2-ylidene
$C_{15}H_{21}BNP$	(trimethylammonio(dihydro)borato)diphenylphosphine)
$C_{16}H_{18}N_2O_2S$	(isobutyl(1-naphthylcarbamothioyl)carbamate)
$C_{17}H_{20}N_2S$	(1,3-bis(2,6-dimethylphenyl)thiourea)
$C_{18}H_{14}P$	((2-chlorophenyl)(diphenylphosphine)
$C_{19}H_{15}OP$	(2-diphenylphophino)benzaldehyde)
$C_{20}H_{16}N_4$	5-anilino-2,4-diphenyl-2,4-dihydro-3H-1,2,4-triazol-3-ylidene

$C_{22}H_{19}S_2P$	(2-(2-phenyl-3-(2-theionyl)-4,5,6,7-tetrahydro-2H-isophosphindol-1-yl)thiophene)
$C_{23}H_{30}N_2OS$	(N-((2,6-disopropylphenyl)carbamothioyl)-2,4,6-trimethylbenzamide)
$C_{27}H_{36}N_2$	(1,3-bis(2,6-bis(propan-2-yl)phenyl)-imidazol-2-ylidene)
$C_{27}H_3N_2$	(1,3-bis (2,6-di-isopropylphenyl)imidazol-2-ylidene)
C_2H_3N	acetonitrile
$C_{32}H_{57}NP$	(5-dicyclohexylphosphino)-1-(2,3-di-isopopylphenyl)-2,2,4,4-tetramethyl-3,4-dihydro-2H-pyrrol-1-ium)
$C_{34}H_{40}N_{4y}P$	(1,3-bis(1,3-di-isopropylbenzimidzale-2-ylidene)-1,3-dihydro-2H-isophophindol-2-yl)
$C_{64}H_{78}N_6PS$	(4-[{1,3-bis[2,6-bis(propan-2-yl)phenyl]-4-phenyl-1H-1,2,3-triazol-3-ium-5-yl}(sulfanyl) phosphenyl)-1,3-bis[2,6-bis(propan-2-yl)phenyl]-5-phenyl-1H-1,2,3 triazol-3-iumato)
Hmpt	methylpyruvate thiosemicarbazone
Imt	imidiazolidine-2-thionate
Me_2imt	N,N′-dimethylimizadolidine-2-thicone
Pcy_3	tricyclohexyl phosphine
PMe_3	trimethylphosphine
PPh_3	triphenylphosphine
$C_{12}H_{11}N_3S$	1-phenyl-3-(2-pyridyl)-2-thiourea
p-tolNC	o-totylcyanide
Py	pyridine
py2SH	pyridine-2-thione
pymtH	pyrimidine-2-thione
tclH	2-thioxohexamethyleneimine
Thm	thiamine
P(o-totyl)$_3$	tri(o-totyl)phosphine
Tuc	thiouracil

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