Copper(I) Halide Complexes with Triphenylphosphane and Heterocyclic Thione Ligands: The Crystal Structures of [Bis(Triphenylphosphane)(Benzimidazole-2-Thione)Copper(I) Iodide], [Bis(Triphenylphosphane)(Benzothiazole-2-Thione)Copper(I) Iodide], and Bis[μ-*S*-(Benzimidazole-2-Thione)(Triphenylphosphane)Copper(I) Chloride]

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Dedicated to Prof. Joseph Grobe on the occasion of his 70th birthday

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While the reaction of benz-1,3-imidazole-2-thione (bzimtH$_2$) or benz-1,3-thiazole-2-thione (bztztH) with copper(I) iodide in the presence of two equivalents of triphenylphosphane led to mononuclear complexes of the type [CuI(PPh$_3$)$_2$(L)], the reaction of benz-1,3-imidazole-2-thione with copper(I) chloride gave a dimeric complex [CuCl(PPh$_3$)(bzimtH$_2$)]$_2$. These three compounds were characterized by IR, UV/Vis, and ^{1}H NMR spectroscopy, and the crystal structures determined by single-crystal X-ray diffraction methods. Vibrational, electronic, and ^{1}H NMR spectroscopic data of the complexes are discussed in relation to the structures.

Introduction

The great interest, currently in copper(I) coordination chemistry is due to the participation of this cation in certain biochemical redox reactions,[1] and also because of its ability to adopt various coordination modes.[2] With tertiary phosphanes as ligands, copper(I) halides produce complexes with ligand to copper halide ratios 2:1, 2:2, 3:1, 3:2, 4:2, and 4:4, with the geometry normally being determined by steric rather than by electronic properties of the phosphane ligands.[3]

During our previous work on the interaction of univalent group IB metal cations with biologically interesting molecules, a number of mixed-ligand coordination compounds of copper(I) halides with heterocyclic thiones and triarylphosphanes were prepared and structurally characterized.[4,5] In these complexes, the neutral thione molecules with both nitrogen and sulfur as donating atoms always adopted the monodentate coordination mode, binding the metal centres exclusively through the exocyclic sulfur atom in a terminal or bridging mode. Nonetheless, a remarkable variety of structures ranging from mononuclear three or four-coordinate species with trigonal planar and tetrahedral Cu(I), respectively, to dimers with pseudo-tetrahedral geometry formed by bridging halogen or thione ligands was obtained, even within a closely related series of thione ligands.[6]

As for the factors governing the stoichiometric and structural preferences of these complexes, the bulk of the ligands seemed to be the main factor that determined the coordination number of the metal atom, since the steric demands of the *ortho*-methyl groups clearly lead to three-coordination in the copper(I) halide complexes of tri-*o*-tolylphosphane.[6] On the other hand, the interplay of several other parameters like the geometrical flexibility of the coinage metals, electronic properties on the part of the ligands, as well as the preparation conditions might also be expected to be of major importance, causing significant changes to the coordination geometry of the metal atom. Thus, for example, the cause of dimerization as well as the reasons for the formation of two different types of binuclear copper(I) halide complexes of general formula [CuX(PR$_3$)thione]$_2$, in which the two copper centers are linked either by a double halide or by a double thione-sulfur bridge, are still not fully understood. On the basis of our earlier observations on dimeric species of the above-mentioned type, the coordination

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behavior (terminal or bridging mode) of each ligand seems to depend on the nature of the halogen present. In particular, formation of halogen-bridges has been found to be preferred for the "soft" iodine but not for the "harder" chlorine base,[7,8,9] whereas both bridging and terminal bonding modes were observed for bromo ligands[10,11] since bromide lies on the borderline between soft and hard. However, the information obtained so far is insufficient to establish the above supposition, so we now report on the synthesis and X-ray crystal structure of three novel copper(I) halide complexes in an attempt to obtain further insight into this problem.

Results and Discussion

General Considerations

The complexes were prepared by reacting equimolar quantities of copper(I) halide and triphenylphosphane (PPh_3) followed by the addition of one equivalent of the appropriate thione (L) in dry acetonitrile solution. This procedure, frequently used for the preparation of copper(I) halide complexes containing both heterocyclic thiones and triphenyl- or tritolylphosphane ligands, gave, in the case of copper(I) iodide, the monomeric complexes [$CuI(PPh_3)_2(bzimtH_2)$] (**1**) and [$CuI(PPh_3)_2(bztztH)$] (**2**). In contrast, copper(I) chloride, used exactly in the same manner, gave the dimer [$CuCl(PPh_3)(bzimtH_2)$]$_2$ (**3**) with the two copper centres being double bridged by the thione-S atom.

Crystals of the complexes, prepared by slow evaporation of the solution remaining after filtration of the initial product deposited from the reactions, were coloured solids, soluble in chloroform, methanol, ethanol, acetone, and acetonitrile. They were stable to air and moisture, and could be manipulated in air after their isolation without appreciable decomposition. Their solutions were non-conducting in acetone and chloroform. Room temperature magnetic measurements confirmed the diamagnetic nature of the compounds.

The electronic absorption spectra of the three complexes in chloroform, which are very similar, are dominated by two broad bands with maxima at 240 nm and in the 310−340 nm region. The first one can be attributed to intraligand transitions of the phosphane ligand, since the uncoordinated triphenylphosphane reveals a strong absorption at 245 nm, which usually remains non-shifted upon coordination to Cu^I.[12,13] The lower energy band lies in the region where the free thiones absorb, expressing a small red shift as a consequence of the coordination to Cu^I and should therefore be considered as a thione-originating intraligand transition with some MLCT character.[12,13]

The infrared spectra of the compounds, recorded in the range 4000−250 cm^{-1} show, apart from the existence of strong phosphane bands, the usual four "thioamide bands" required by the presence of the heterocyclic thione ligands, as well as the characteristic NH stretching vibrations observed in the 3050−3160 cm^{-1} region. The shifts observed for these bands due to coordination (upward shifts of 15−35 cm^{-1} for thioamide I, downward shifts of 10−30 cm^{-1} for thioamide II and III) in combination with the lack of ν(SH) bands at ca. 2500−2600 cm^{-1}, signify the exclusive S-coordination mode of the thione ligands.

The prevalence of the thione tautomer in the complexes is further confirmed by the ^1H NMR spectra of the compounds, which display, apart from the signals expected for the phosphane and thione ligands, a single resonance at $\delta \approx$ 12−14, attributed to the NH proton.

Description of the Structures

[$CuI(PPh_3)_2(bzimtH_2)$] (1) and [$CuI(PPh_3)_2(bztztH)$] (2)

The main bond lengths and angles for compounds **1** and **2** are given in Tables 1 and 2. Molecular plots showing the atom numbering schemes are shown in Figures 1 and 2, re-

Table 1. Selected bond lengths [Å] and angles [°] for **1**

Cu(1)−P(1)	2.2839 (10)	P(1)−C(14)	1.831 (3)
Cu(1)−P(2)	2.2796 (9)	P(1)−C(20)	1.818 (3)
Cu(1)−S(1)	2.3692 (9)	P(2)−C(26)	1.827 (3)
Cu(1)−I(1)	2.6901 (6)	P(2)−C(32)	1.826 (3)
S(1)−C(1)	1.691 (3)	P(2)−C(38)	1.828 (3)
P(1)−C(8)	1.834 (3)		
P(2)−Cu(1)−P(1)	122.45(4)	C(14)−P(1)−Cu(1)	114.16(10)
P(2)−Cu(1)−S(1)	104.55(3)	C(8)−P(1)−Cu(1)	113.46(11)
P(1)−Cu(1)−S(1)	105.97(3)	C(32)−P(2)−C(26)	101.23(13)
P(2)−Cu(1)−I(1)	105.70(3)	C(32)−P(2)−C(38)	103.76(13)
P(1)−Cu(1)−I(1)	106.14(3)	C(26)−P(2)−C(38)	103.76(13)
S(1)−Cu(1)−I(1)	112.10(3)	C(32)−P(2)−Cu (1)	114.83(10)
C(20)−P(1)−C(14)	104.63(14)	C(26)−P(2)−Cu(1)	117.99(9)
C(20)−P(1)−C(8)	104.03(14)	C(38)−P(2)−Cu(1)	113.88(10)
C(14)−P(1)−C(8)	103.42(14)	C(1)−S(1)−Cu(1)	111.34(10)
C(20)−P(1)−Cu(1)	115.80(10)		

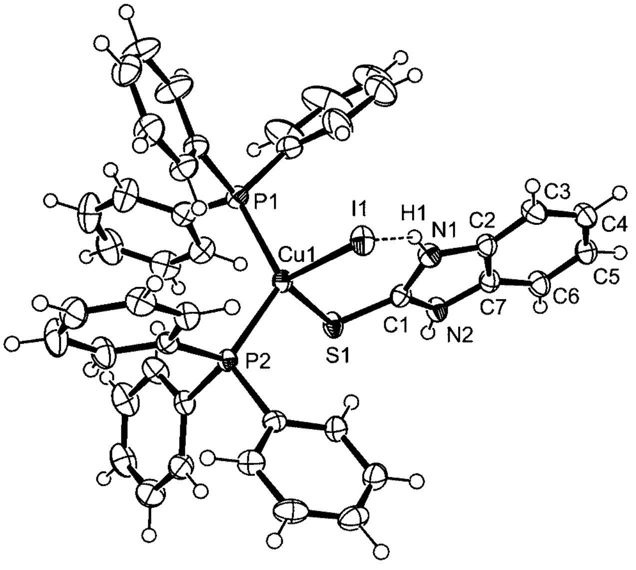

Figure 1. A view of compound **1** with atom labels. Displacement ellipsoids are shown at the 50% probability level

spectively, and details of the hydrogen bonding are shown in Table 3. Both complexes are mononuclear with the copper atom being surrounded by two P, one S, and one I atom in a distorted tetrahedral coordination. It should be noted that copper(I) iodide usually tends to form dimeric complexes with two iodine atoms serving as bridges between the two copper atoms, while only one single representative of mononuclear species with a $CuIP_2S$ core exists among the structures characterized by us so far.[5] The largest deviation from the ideal geometry is reflected by the P−Cu−P angles with values of 122.45(4)° (**1**) and 125.33(2)° (**2**). These higher angles are counterbalanced by the bond angles I−Cu−P(1), I−Cu−P(2), S−Cu−P(1), and S−Cu−P(2), whose values are all lower than the tetrahedral value of 109.4°. This tetrahedral distortion may be attributed to steric interactions between the bulky phosphane ligands, which is common among a large series of monomeric copper(I) halide complexes containing one heterocyclic thione and two monodentate triphenylphosphane ligands, and exhibiting the same $CuSP_2X$ core.[11,14,15]

Table 2. Selected bond lengths [Å] and angles [°] for **2**

Cu(1)−P(1)	2.2822 (6)	P(1)−C(14)	1.818 (2)
Cu(1)−P(2)	2.2796 (6)	P(1)−C(20)	1.827 (2)
Cu(1)−S(1)	2.3660 (6)	P(2)−C(26)	1.822 (2)
Cu(1)−I(1)	2.6807 (3)	P(2)−C(32)	1.832 (2)
S(1)−C(1)	1.668 (2)	P(2)−C(38)	1.830 (2)
P(1)−C(8)	1.824 (2)		
P(2)−Cu(1)−P(1)	125.33(2)	C(8)−P(1)−C(20)	101.74(10)
P(2)−Cu(1)−S(1)	104.44(2)	C(14)−P(1)−Cu(1)	115.99(7)
P(1)−Cu(1)−S(1)	98.82(2)	C(8)−P(1)−Cu(1)	113.97(7)
P(2)−Cu(1)−I(1)	107.053(17)	C(20)−P(1)−Cu(1)	112.95(7)
P(1)−Cu(1)−I(1)	108.907(18)	C(26)−P(2)−C(38)	103.53(10)
S(1)−Cu(1)−I(1)	111.740(18)	C(26)−P(2)−C(32)	102.60(9)
C(1)−S(1)−Cu(1)	115.65(8)	C(38)−P(2)−C(32)	102.86(10)
C(2)−S(2)−C(1)	91.69(11)	C(26)−P(2)−Cu(1)	111.53(7)
C(14)−P(1)−C(8)	104.79(10)	C(38)−P(2)−Cu(1)	116.77(7)
C(14)−P(1)−C(20)	106.03(10)	C(32)−P(2)−Cu(1)	117.68(7)

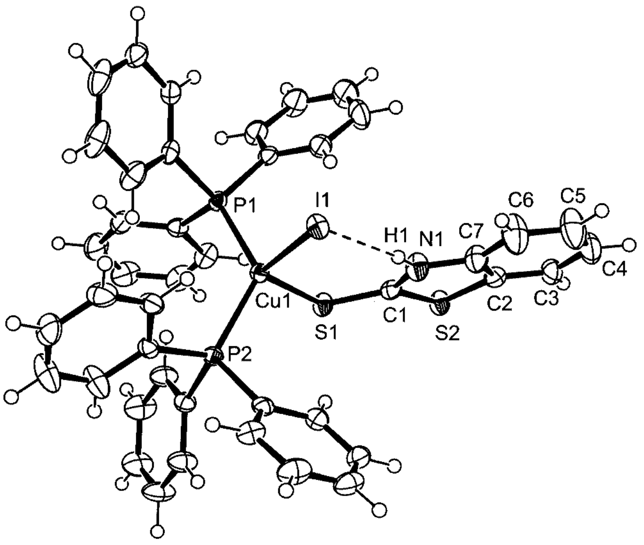

Figure 2. A view of compound **2** with atom labels. Displacement ellipsoids are shown at the 50% probability level

Table 3. Selected bond lengths [Å] and angles [°] for **3**

Cu(1)−P(1)	2.236(3)	P(1)−C(8)	1.813(9)
Cu(1)−S(1)^{1} [a]	2.332(2)	P(1)−C(20)	1.819(8)
Cu(1)−C1(1)	2.347(2)	P(1)−C(14)	1.855(8)
Cu(1)−S(1)	2.555(3)	P(2)−C(33)	1.828(9)
Cu(1)−Cu(1)^{1}	2.919(2)	P(2)−C(45)	1.840(8)
Cu(2)−P(2)	2.234(3)	P(2)−C(39)	1.844(9)
Cu(2)−S(2)^{2}	2.352(3)	N(1)−C(1)	1.366(10)
Cu(2)−Cl(2)	2.357(2)	N(1)−C(2)	1.378(10)
Cu(2)−S(2)	2.448(3)	N(2)−C(1)	1.342(10)
Cu(2)−Cu(2)^{2}	2.943(2)	N(2)−C(7)	1.381(10)
S(1)−C(1)	1.708(8)	N(3)−C(26)	1.326(12)
S(1)−Cu(1)^{1}	2.332(2)	N(3)−C(27)	1.391(11)
S(2)−C(26)	1.745(10)	N(4)−C(26)	1.363(12)
S(2)−Cu(2)^{2}	2.352(3)	N(4)−C(32)	1.409(12)
P(1)−Cu(1)−S(1)^{1}	116.05(10)	P(2)−Cu(2)−Cu(2)^{1}	134.28(8)
P(1)−Cu(1)−Cl(1)	114.53(9)	S(2)^{1}−Cu(2)−Cu(2)^{2}	53.67(7)
S(1)^{1}−Cu(1)−Cl(1)	112.81(9)	Cl(2)−Cu(2)−Cu(2)^{2}	119.05(10)
P(1)−Cu(1)−S(1)	110.90(9)	S(2)−Cu(2)−Cu(2)^{2}	50.71(7)
S(1)^{1}−Cu(1)−S(1)	106.79(7)	C(1)−S(1)−Cu(1)^{1}	107.7(3)
Cl(1)−Cu(1)−S(1)	93.06(8)	C(1)−S(1)−Cu(1)	110.4(3)
P(1)−Cu(1)−Cu(1)^{1}	131.53(8)	Cu(1)^{1}−S(1)−Cu(1)	73.21(7)
S(1)^{1}−Cu(1)−Cu(1)^{1}	56.92(7)	C(26)−S(2)−Cu(2)^{2}	105.7(3)
Cl(1)−Cu(1)−Cu(1)^{1}	110.88(9)	C(26)−S(2)−Cu(2)	105.2(4)
S(1)−Cu(1)−Cu(1)^{1}	49.87(6)	Cu(2)^{2}−S(2)−Cu(2)	75.62(8)
P(2)−Cu(2)−S(2)^{2}	116.23(9)	C(8)−P(1)−Cu(1)	117.7(3)
P(2)−Cu(2)−Cl(2)	105.96(10)	C(20)−P(1)−Cu(1)	111.5(3)
S(2)^{2}−Cu(2)−Cl(2)	112.93(10)	C(14)−P(1)−Cu(1)	117.6(3)
P(2)−Cu(2)−S(2)	114.52(9)	C(33)−P(2)−Cu(2)	114.7(3)
S(2)^{2}−Cu(2)−S(2)	104.38(8)	C(45)−P(2)−Cu(2)	112.5(3)

[a] Symmetry transformations used to generate equivalent atoms: #^{1}: $-x + 1, -y + 1, -z + 1$; #^{2}: $-x, -y, -z$.

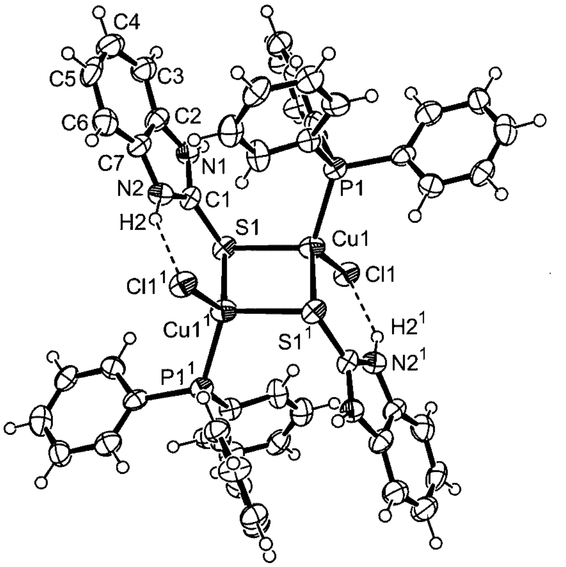

Figure 3. A view of compound **3** with atom labels. Displacement ellipsoids are shown at the 50% probability level

The Cu−I and Cu−S bonds in **1** and **2** are both somewhat longer, while the two individual Cu−P distances are

Table 4. Hydrogen bonding in the three complexes

Compd.	Donor (D)	H	Acceptor (A)	DH [Å]	HA [Å]	DA [Å]	DHA [°]
1	N1	H1	I1	0.88	2.73	3.526(2)	151
1	N2	H2	O1$^{\mathbf{i}}$ [a]	0.88	2.06	2.860(3)	150
2	N1	H1	I1	0.88	2.63	3.493(2)	167
2	C31	H31	S1	0.95	2.87	3.719(2)	149
2	C40	H40	S1$^{\mathbf{ii}}$	0.95	2.83	3.648(2)	146
3	N1	H1	Cl2$^{\mathbf{iii}}$	0.88	2.56	3.227(7)	133
3	N2	H2	Cl1$^{\mathbf{iv}}$	0.88	2.30	3.105(7)	153
3	N3	H3	Cl2$^{\mathbf{v}}$	0.88	2.18	3.036(8)	165
3	N4	H4	Cl1	0.88	2.36	3.198(9)	159
3	C15	H15	N2	0.95	2.48	3.25(1)	137
3	C49	H49	Cl1	0.95	2.80	3.53(1)	134

[a] Atom coordinates transposed by: **i**: x, $0.5 - y$, $0.5 + z$; **ii**: $-1 + x$, y, z; **iii**: $1 - x$, $1 - y$, $1 - z$; **iv**: $-x$, $1 - y$, $-z$; **v**: $1 + x$, y, z.

slightly shorter than those found in [CuI(PPh$_3$)$_2$(pymtH)]. This represents, according to the Cambridge Structural Database, a unique known structure of a monomeric, tetrahedrally coordinated copper(I) iodide complex with terminal iodine and thione-sulfur donors.[5] These bond lengths all lie within the range of the corresponding values previously reported for a number of related tetracoordinated copper(I) complexes.

[CuCl(PPh$_3$)(bzimtH$_2$)]$_2$ (3)

The asymmetric unit of the crystal cell contains two half-molecules. The atoms in molecule **3a** are Cu1, S1, Cl1, C1−C25, H1, H2, H3A, H4A, H5−H24, and their equivalent primed atoms. The atoms in molecule **3b** are Cu2, S2 Cl2, N3, N4, C26−C50, H3, H4, H26−H50, and their equivalent primed atoms. The main bond lengths and angles for both molecules are given in Table 4, and an ORTEP view of molecule **3a** showing the atom numbering is given in Figure 3. There are some significant differences in bond lengths and angles between the two molecules which will be mentioned in the subsequent discussion. The basic structural unit of [CuCl(PPh$_3$)(bzimtH$_2$)]$_2$ is a dimer in which the two copper atoms are doubly bridged by two S atoms of the thione ligands to form a strictly planar four-membered Cu$_2$S$_2$ core. The slightly distorted tetrahedral coordination around copper is completed by one P atom from the phosphane ligand and one chlorine atom.

Three structurally determined analogues, [CuCl(tmtp)(bzimtH$_2$)]$_2$ (tmtp = tri-*m*-tolylphosphane), [CuCl(tptp)(tzdtH)]$_2$ (tptp = tri-*p*-tolylphosphane, tzdtH = 1,3-thiazolidine-2-thione), and [CuCl(tptp)(pmtH)]$_2$ (pmtH = pyrimidine-2-thione) will be used for the subsequent comparative discussion (hereafter referred to as complexes **A**, **B**, and **C**, respectively).

Each of the two non-equivalent Cu−S bonds of 2.332(2) and 2.555(3) Å in **3a** and 2.322(3) and 2.448(3) Å in **3b**, respectively, are within the range expected for binuclear Cu^{I} complexes with double bridging sulfur atoms. The asymmetry in the two bridging distances in molecule **3a**, however, is remarkably larger than in the three already known analogues. As in the other dimers, the two bulky phosphane ligands are *trans* disposed with a Cu−P bond length of 2.236(3) Å, somewhat longer than the values observed in **B** and **C**, but clearly shorter than the "long" one [2.251(1) Å] in **A**. Likewise, the Cu−Cl bond length of 2.347(2) Å in **3a** and 2.357(2) Å in **3b**, lies well above the corresponding values 2.283(1) and 2.300(1) Å found in **C** and **B**, but is significantly shorter than that in **A** [2.391(2) Å]. As previously demonstrated, this Cu−Cl bond appears to be associated with the S−Cu−S angle, namely an opening up of the S−Cu−S angle from 92.48(2)° in **B** to 93.24(2)° in **C** and 110.2(1)° in **A** results in an elongation of the Cu−Cl bond.[16] As for the complex under consideration, it fits well into the above mentioned series, even when the mean values for the Cu−Cl bond length and the S−Cu−S angle for **3a** and **3b** are taken into consideration.

The S−Cu−S and Cu−S−Cu angles [106.79(7) and 73.21(7)° for **3a** and 104.38(8) and 75.62(8)° for **3b**], which are close to the ideal values (109.5 and 70.5°) for symmetric dimers, deviate significantly from those found in **B** and **C**, but are not far from those observed in **A**. The value of the Cl−Cu−S angle of 102.10(10)° in **3b** is similar to the corresponding values observed in the previous complexes **B** and **C**, whereas the same angle in **3a** [93.06(8)°] is strongly distorted and very close to that observed in complex **A**. Finally, the value of the P−Cu−Cl angle of 114.53(9)° in **3a** is similar to the corresponding values observed in the previous complexes **A**, **B**, and **C**, but the same angle in **3b** is surprisingly much smaller [105.96(10)°].

Computational Study

It is generally accepted that the local metal environment in monovalent copper coordination compounds is mainly determined by steric effects as well as by the Lewis basicity of the ligands, but additional considerations may be useful in explaining the situation in some specific cases. The dimerization often realized in copper(I) halide complexes containing heterocyclic thione and triarylphosphane ligands as well as the bridging or terminal bonding mode of each ligand in such dimers, for instance, are of unknown origin. The contribution of electronic factors, however, is suspected to be important. The computations performed in the present paper are an attempt to unravel any such electronic factor.

The lowest unoccupied molecular orbitals (LUMO) for **3A** and **3B** are 3.346 eV and 3.349 eV higher, respectively, than their highest occupied molecular orbitals (HOMO), while the LUMO energies in complexes **2** and **1** are higher than their HOMO energies by 3.518 and 3.432 eV, respect5ively. This indicates that the monomers are more stable than the dimers. An overlap population of 0.005 e in **3A** and 0.001 e in **3B** between the two metal centres, which are separated by 2.919(2) Å and 2.943(2) Å, respectively, has been calculated for the dimeric structures, whereby the corresponding value for $\mathrm{[CuI(pytH)(tmtp)]_2}$,[9] with a Cu···Cu distance of 3.119(1) Å, was found to be 0.006 e. The bonding nature of these metal−metal interactions is, of course, too small to be considered as the crucial factor for the domination of the dimeric structures. The stabilizing effect of a metal−metal interaction could be important only for Cu···Cu separations below the value of 2.80 Å proposed to be the sum of two copper covalent van der Waals radii. In the case of $\mathrm{[CuCl(bztzdtH)(tmtp)]_2}$ or $\mathrm{[CuBr(pytH)(tmtp)]_2}$,[16] where the Cu···Cu distances are 2.764 and 2.691 Å (both shorter than the sum of the copper−copper van der Waals radius by 0.046 and 0.109 Å, respectively), the corresponding overlap populations are 0.019 e and 0.026 e.

The calculated overlap populations for the Cu(1)−S(1) and Cu(1)−S(1)^1 bonds in **3** are 0.384 e and 0.178 e, respectively. The calculated overlap populations for the Cu(1)−P(1) and Cu(1)−Cl(1) bonds are 0.607 and 0.330 e, respectively. The calculated overlap populations, for the Cu(1)−I(1) and Cu(1)−S(1) bonds are 0.244 and 0.348 e, respectively, in complex **2** and 0.255 and 0.344 e in complex **1**, while the values for the overlap population calculated for the two Cu(1)−P(1) and Cu(1)−P(2) bonds are 0.566 and 0.565 e in complex **2** and 0.561 and 0.571 e, respectively, in complex **1**.

Conclusion

The coordination chemistry of copper(I) with heterocyclic thiones and tertiary phosphanes as ligands offers opportunities for the detailed examination of the factors governing the stereochemical preferences of copper(I) compounds. According to our previous investigations, the stoichiometry may be one of these factors, especially in association with the solvent used for the preparation. The three new copper(I) complexes investigated in this work were prepared in an acetonitrile/methanol mixture, whereby two different types of structures were formed, tetrahedral monomeric and pseudo-tetrahedral dimeric with the halogen acting as bridging ligand. However,

Table 5. Crystal data and structure refinement

	1	**2**	**3**
Chemical formula	$\mathrm{C_{43}H_{36}CuIN_2P_2S{\cdot}CH_3OH{\cdot}0.85CH_3CN{\cdot}0.27H_2O}$	$\mathrm{C_{43}H_{35}CuINP_2S_2}$	$\mathrm{C_{50}H_{42}Cl_2Cu_2N_4P_2S_2}$
Molecular weight	934.4	882.22	1022.92
Temperature	150(2) K	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a	12.528(3) Å	9.6250(10) Å	12.4251(8) Å
b	18.573 (4) Å	22.9400 (10) Å	13.6559 (10) Å
c	18.639 (4) Å	17.9130 (10) Å	13.9637 (13) Å
α	90°	90°	95.533 (3)°
β	91.49 (3)°	95.025 (5)°	91.756 (3)°
γ	90°	90°	104.047 (7)°
Volume	4335.7 (15) Å^3	3939.9 (5) Å^3	2284.2 (3) Å^3
Z	4	4	2
Density (calculated)	1.424 Mg/m^{3}Å	1.487 Mg/m^{3}Å	1.487 Mg/m^{3}Å
Absorption coefficient	1.375 mm^{-1}	1.556 mm^{-1}	1.250 mm^{-1}
$F(000)$	1873	1776	1048
Crystal size	0.24 × 0.22 × 0.06 mm	0.34 × 0.22 × 0.18 mm	0.07 × 0.05 × 0.01 mm
Theta range for data collection	2.27 to 27.48°	2.28 to 27.48°	2.43 to 25.06°
Index ranges	$-16 \le h \le 15$	$-12 \le h \le 12$	$-14 \le h \le 14$
	$-21 \le k \le 24$	$-26 \le k \le 29$	$-16 \le k \le 16$
	$-24 \le l \le 24$	$-22 \le l \le 23$	$-16 \le l \le 16$
Reflections collected	37460	34765	25382
Independent reflections	9838 [R(int) = 0.0525]	8940 [R(int) = 0.0484]	7977 [R(int) = 0.1828]
Completeness to theta = 27.48°	99.0%	98.8%	98.5%
Data [$I > 2\sigma(I)$] / restrains / parameters	7872 / 6 / 481	7266 / 0 / 452	3776 / 0 / 559
Max. and min. transmission	0.9220 and 0.7337	0.7670 and 0.6197	0.9876 and 0.9176
Refinement method	Full-matrix l.s. on F^2	Full-matrix 1.s. on F^2	Full-matrix 1.s. on F^2
Goodness-of-fit on F^2	1.024	1.039	0.945
Final R indices [$I > 2\sigma(I)$]	$R1=0.0390$, $wR2=0.0999$	$R1=0.0315$, $wR2=0.0727$	$R1=0.0784$, $wR2=0.1710$
R indices (all data)	$R1=0.0547$, $wR2=0.1091$	$R1=0.0452$, $wR2=0.0775$	$R1=0.1873$, $wR2=0.2203$
Final weighting scheme	Calc $w = 1/[\sigma^2(F_0^2) + (0.0582P)^2 + 4.5196P)$, where $P = (F_0^2 + 2F_c^2)/3$	Calc $w=1/[\sigma^2(F_0^2) + (0.0420P)^2 + 0.0789P)$, where $P = (F_0^2 + 2F_c^2)/3$	Calc $w = 1/[\sigma^2(F_0^2) + (0.0989P)^2 + 0.0000P)$, where $P = (F_0^2 + 2F_c^2)/3$
Largest diff peak and hole	1.103 and −1.496 e/Å^3	0.488 and −1.240 e/Å^3	0.823 and −0.597 e/Å^3

since the softness of the halogen decisively affects its donor properties, reaction stoichiometry and solution media cannot be considered as the only reason for the structural preferences of copper(I), at least in the case of complexes investigated in this work. Consequently, this phenomenon needs more extensive studies in consideration of further structures of this series. Finally, extended Hückel calculations could not provide any evidence for significant interaction between the two copper(I) centres, despite the short Cu−Cu distance, in the case of the dimeric complex $[CuCl(PPh_3)(bzimtH_2)]_2$ (**3**).

Experimental Section

Materials and Instruments: Copper(I) chloride, copper(I) iodide, and all solvents are commercially available and were used as obtained, while the thiones (Merck or Aldrich) were recrystallized from hot ethanol prior to their use. Elemental analyses for C, H, N, and S were carried out with a Carlo erba EA MODEL 1108. Melting points were measured in open tubes with a STUART scientific instrument and are uncorrected. Infra-red spectra in the region of 4000−370 cm^{-1} were obtained in KBr discs while far-infrared spectra in the region of 400−50 cm^{-1} were obtained in polyethylene discs, with a Perkin−Elmer Spectrum GX FT-IR spectrometer. A Jasco UV/Vis/NIR V 570 series spectrophotometer was used to obtain the electronic absorption spectra.

Computational: Extended Hückel calculations were performed using the CACAO program.[17] The calculations were carried out using crystallographic data from the studied molecules. The EHT parameters for Cu were those established in the literature.

Synthesis of the Complexes: The complexes were prepared according to the following general procedure. A suspension of copper(I) halide (0.5 mmol) and triphenylphosphane (132 mg, 0.5 mmol) in 10 cm^3 of acetonitrile was stirred until a white precipitation of the intermediate $[Cu_nX_n(PPh_3)_m]$ (X = Cl or I) complex was formed. A solution of the appropriate thione (0.5 mmol beznimidazoline-2-thione (bzimtH) or benzthiazoline-2-thione (bztzdtH) in methanol was then added and the new suspension was stirred until clear (15 min). The resulting solution was filtered off and the clear solution was kept in darkness at room temperature. After 24 hours, crystals of the complexes suitable for single crystal analysis by X-ray crystallography were obtained by filtration.

$[CuI(PPh_3)_2(bzimtH)]$ (1): Pale yellow crystals. Yield 340 mg (72%), m.p. 221−222 °C; $C_{43}H_{36}CuIN_2P_2S{\cdot}CH_3OH{\cdot}0.85CH_3CN{\cdot}0.27H_2O$: C 59.36, H 4.77, N 4.42; found C 59.55, H 4.63, N 4.30%. IR $\tilde{\nu}$ (cm^{-1}): 3050 w, 1619 m, 1493 s, 1434 vs, 1161 s, 1093 s, 742 vs, 694 vs, 603 s, 517 vs, 490 vs; far-IR $\tilde{\nu}$ (cm^{-1}): 218 m, 200 m, 174 s, 162 s, 151vs, 146 m, 121 s. UV-Vis, λ_{max} (logε), $CHCl_3$: 241 (4.373), 310 (4.412).

$[CuI(PPh_3)_2(bztzdtH)]$ (2): Orange crystals. Yield 335 mg (76%), m.p. 218−219 °C; $C_{43}H_{35}CuINP_2S_2$: C 58.54, H 3.99, N 1.59; found C 58.84, H 3.88, N 1.70%. IR $\tilde{\nu}$ (cm^{-1}): 3052 w, 1488 s, 1424 vs, 1322 s, 1094 s, 1029 s, 743 vs, 695 vs, 515 vs, 503 vs; far-IR $\tilde{\nu}$ (cm^{-1}): 219 m, 205 m, 200 m, 174 s, 164 s, 151 vs, 146 m, 121 s. UV-Vis, λ_{max} (logε), $CHCl_3$: 243 (4.471), 329.5 (4.304).

$[CuCl(PPh_3)(bzimtH)]_2$ (3): Pale yellow crystals. Yield 395 mg (77%), m.p. 249−250 °C; $C_{50}H_{42}Cl_2CuN_2P_2S_2$: C 58.71, H 4.13, N 5.48; found C 58.79, H 4.01, N 5.52%. IR $\tilde{\nu}$ (cm^{-1}): 3193 m, 3053 s, 1502 vs, 1459 vs, 1446 s, 1179 vs, 1095 s, 743 vs, 694 vs, 598 s, 520 vs, 501 vs; far-IR $\tilde{\nu}$ (cm^{-1}): 217 w, 200 w, 174 s, 163 s, 151 vs, 146 m, 121 s. UV-Vis, λ_{max} (logε), $CHCl_3$: 240.5 (4.358), 310.5 (4.530).

X-ray Crystallographic Study: The unit cell and intensity data were collected on a Delft Instruments FAST diffractometer using the routines ENDEX, REFINE, and MADONL in the MADNES software suite[18] and processed using ABSMAD;[19] detailed procedures are described by Darr, Drake, Hursthouse, and Malik.[20] Absence of crystal decay in the X-ray beam was confirmed by checking equivalent reflections at the beginning and end of data collection, which lasted about 8 hours. The structures were solved with SIR92[21] and refined with SHELX93.[22] Details are given in Table 5. The copper, bromine, chlorine, iodine, sulfur, phosphorus, nitrogen, and carbon atoms were refined with anisotropic temperature factors. The hydrogen atoms were allowed to ride on their attached atoms with common isotropic temperature factors for methyl and non-methyl hydrogens. An absorption correction was made with DIFABS.[23]

CCDC-174528 (**1**), -174529 (**2**), and -174526 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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