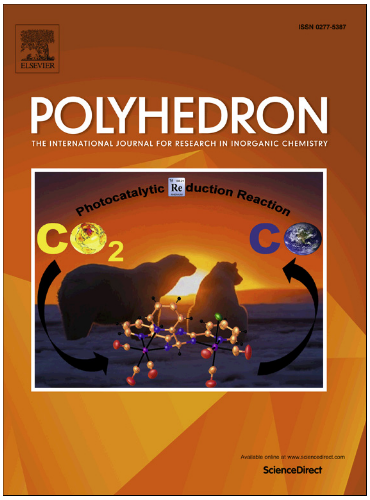

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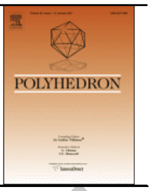

# Complexation of tris(2-pyridyl)phosphine chalcogenides with copper(I) halides: the selective formation of scorpionate complexes, [Cu(*N*,*N*′,*N*″-2-Py$_3$P=X)Hal] (X = O, S and Se)

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ABSTRACT

A series of copper(I) scorpionates, [Cu(*N*,*N*′,*N*″-2-Py$_3$P=X)Hal] (X = O, S and Se; Hal = Cl, I), has been synthesized in 67-88% yields by the reaction of tris(2-pyridyl)phosphine chalcogenides with Cu(I) halides ($CH_2Cl_2$, r.t., 10 min). These complexes were characterized by X-ray crystallography, NMR and UV-Vis techniques to reveal that the ligand coordinates with Cu(I) ion *via* three pyridine nitrogen atoms to form near-*C*$_3$-symmetrical [Cu(N-C)$_3$P=X] cage. The halogen atoms are bonded with metal so that the latter adopts a distorted trigonal pyramidal geometry. The DFT computations confirm that the observable $\kappa^3$-*N*,*N*′,*N*″-binding of the ligands is energetically more favorable than the alternative coordination modes, i.e. $\kappa^1$-*X*-monodentate, $\kappa^2$-*N*,*N*′- or $\kappa^2$-*N*,*X*-bidentate and $\kappa^3$-*N*,*N*′,*X*-tridentate.

## 1. Introduction

Over the last decade, pyridylphosphines have gained much popularity due to their wide application, mainly as remarkable *P*,*N*-hemilabile ligands in coordination chemistry and catalysis [1]. Among them, tris(2-pyridyl)phosphine is of special interest, especially after the recent development of convenient method for its synthesis directly from elemental phosphorus and 2-bromopyridine [2] that makes this phosphine and, hence its chalcogenides, easily accessible ligands. Owing to its unique structure [3], tris(2-pyridyl)phosphine exhibits rich coordination capabilities forming a variety of complexes [1,4], many of which show catalytic activity [5].

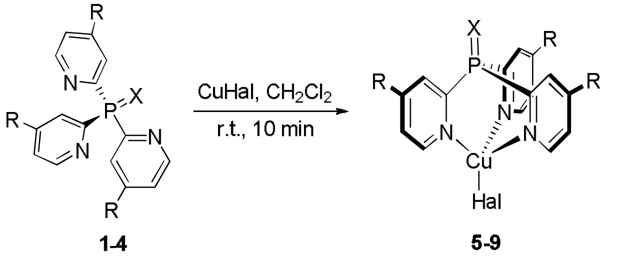
On the other hand, the coordination chemistry of tris(2-pyridyl)phosphine chalcogenides (TPPCs) is poorly investigated, though they are highly promising ligands. The vicinal disposition of the three pyridine N atoms toward the chalcogen atom (O, S or Se) within TPPCs provides the great possibility to assemble complexes with diverse architectures *via* alteration of metal centers, metal-to-ligand ratio and reaction conditions. The TPPC complexes, apart from their importance in material science and catalysis, can be interesting objects for medicinal chemistry since both phosphine chalcogenide complexes [6] and pyridine-based ones [7] are known to exhibit pharmaceutical activity. Nevertheless, complexes with TPPCs are scarce. Thus, only several sandwich [Fe($\kappa^3$-*N*,*N*′,*N*″-Py$_3$P=O)$_2$] [8] and semi-sandwich [M($\kappa^3$-*N*,*N*′,*N*″-Py$_3$P=O)] (M = W [9] and Rh [10]) complexes have been prepared from tris(2-pyridyl)phosphine oxide. Besides, [Mo($\eta^3$-allyl)Br(CO)$_2$($\kappa^2$-*N*,*O*-Py$_3$P=O)] [11] and [Rh($\eta^4$-COD)($\kappa^2$-*N*,*N*′-Py$_3$P=O)](BF$_4$) [10] complexes are known. From phosphine sulfide, one Mo(0) [12] and one Pd(II) [13] complexes have been synthesized, in which *N*,*N*′,*S*- and *N*,*S*-coordination, correspondingly, is realized. More recently, we have obtained a series of square-planar complexes [Pd($\kappa^2$-*N*,*N*′-(Py$_3$P=X)Cl$_2$] (X = O, S or Se) in which TPPCs act as *N*,*N*′-bidentate ligands [14].

Herein, we report on complexation of TPPCs with Cu(I) halides. A priori, it was difficult to predict the result of such interaction because the (*i*) TPPCs are multidentate *N*- and *O*(*S*/*Se*)-ligands, and (*ii*) Cu(I) halides are able to form a great number of mono- and, especially polynuclear complexes [15], in which metal can adopts linear, square trigonal and/or tetrahedral geometry.

## 2. Results and Discussion

### *2.1. Synthetic aspects*

We have found that the reaction of CuCl or CuI with 1 equiv. of diverse TPPCs **1**-**4** readily occurs in $CH_2Cl_2$ solution (r.t., 10 min) to selectively give scorpionate complexes **5**-**9** (67-88% isolated yields) in which ligands behave as $\kappa^3$-*N*,*N*′,*N*″-donors (Scheme 1). Notably, despite higher affinity of the S- and Se-donors toward Cu(I) ion [16], only pyridine N atoms of tris(2-pyridyl)phosphine sulfide (**3**) and selenide (**4**) participate in complexation with Cu(I) halides, whereas the P=S and P=Se bonds remain non-coordinated. The alteration of metal/ligand ratio does not change the reaction course, but reduces the yield of products **5**-**9**. The latter are isolated as air-stable garnet crystals, well soluble in organic solvents (acetone, chloroform, acetonitrile) and insoluble in water. In solution, these complexes were characterized by NMR ($^1$H and $^{31}$P) and UV-Vis spectroscopy, while their solid state was studied by X-ray diffraction analysis.

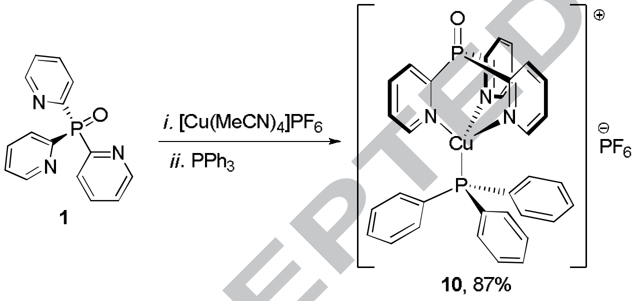


**1**: X = O, R = H;
**2**: X = O, R = Me;
**3**: X = S, R = H;
**4**: X = Se, R = H

**5**: X = O, Hal = Cl, R = H (88%);
**6**: X = O, Hal = I, R = H (72%);
**7**: X = O, Hal = I, R = Me (67%);
**8**: X = S, Hal = I, R = H (75%);
**9**: X = Se, Hal = I, R = H (70%);

**Scheme 1.** Synthesis of complexes **5-9**.

Under the same conditions (r.t., $CHCl_3$, argon), $[Cu(MeCN)_4]PF_6$ appears to be immediately react with the ligand **1** to presumably give cationic scorpionate of $[Cu(\kappa^3\text{-}N,N',N''\text{-}2\text{-}Py_3P{=}O)]PF_6$ type, the $^{31}$P NMR spectrum of which contains two signals, –10.14 (s, $Py_3P{=}O$), –143.82 (quint, $^1J_{PF}$ = 716 Hz, $PF_6$). Upon storage on air, this scorpionate, however, is easily oxidized with dioxygen furnishing paramagnetic green Cu(II) species (thoroughly uninvestigated). Nevertheless, if $Ph_3P$ or $Ph_3As$ is added to orange solution of $[Cu(\kappa^3\text{-}N,N',N''\text{-}2\text{-}Py_3P{=}O)]PF_6$, the $O_2$-stable cationic complexes $[Cu(\kappa^3\text{-}N,N',N''\text{-}2\text{-}Py_3P{=}O)(\kappa^1\text{-}E\text{-}EPh_3)]PF_6$ [E = P (**10**) or As (**11**)] are instantly formed in almost quantitative yields. One of such complexes, namely $[Cu(\kappa^3\text{-}N,N',N''\text{-}2\text{-}Py_3P{=}O)(\kappa^1\text{-}P\text{-}PPh_3)]PF_6{\cdot}2CHCl_3$ (**10**) has been isolated in 89% yield as single crystals suitable for X-ray analysis (Scheme 2). While the crystallographic data of **10** is of low quality, its structural peculiarities are distinct.



**Scheme 2.** Synthesis of complex **10** (*conditions*: $CH_2Cl_2$, r.t.).

## *2.2. UV-Vis and NMR study*

The absorption spectra of complexes **5-9** in $CHCl_3$ solution at 298 K are virtually superimposable (Figure 1). They exhibit intense bands at *ca.* 260 nm which are caused by intraligand $\pi\rightarrow\pi^*$ transitions (within pyridine cycles) since the free ligands display absorptions in the similar region ($\lambda_{max}$ ~ 264 nm). The two broad lower energy bands in regions of 320-345 and 405-470 nm are tentatively assigned to MLCT transitions [17], corresponding to a transition from the HOMO orbital centered in Cu atom ($d^{10}$ full shell) toward a $\pi^*$-orbitals of the ligand.

The $^1$H NMR spectra of complexes **5-9** show four resonance signals of the pyridine protons, shifted downfield from the non-coordinated ligands [18]. Thus, similarly to solid state (*vide infa*), all pyridine cycles in **5-9** remain equivalent in solution. The comparison of the $^1$H NMR spectra for $[Cu(2\text{-}Py_3P{=}O)Cl]$ (**5**) and $[Cu(2\text{-}Py_3P{=}O)I]$ (**6**) reveals that nature of the halogen atoms does not effect on $\delta_H$ values, however, the signals of iodo-complex **6** (similar to **7-9**) being more split. Similarly, within series of one-type complexes **6**, **8** and **9**, the variation of chalcogen atom (O, S, Se) nearly does not change the $^1$H NMR shifts of pyridine protons. The $^{31}$P NMR spectra of **5-9** contain sharp singlets from -9.45 (for **5**) to 11.82 ppm (for **8**), which are shifted upfield by 19-25 ppm with respect to the corresponding free ligand [18].

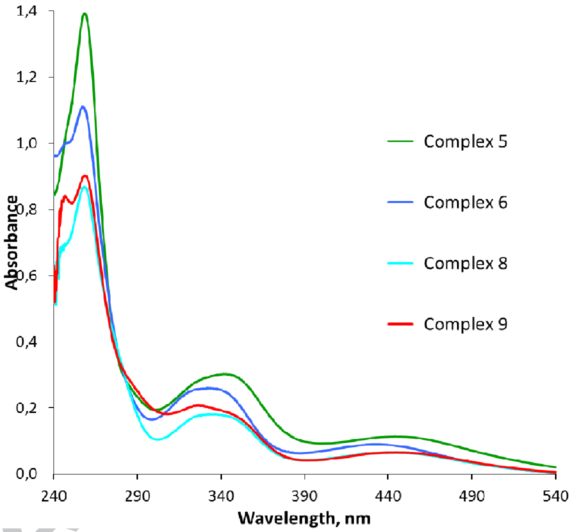


**Fig. 1.** UV-Vis spectra of complexes **5**,**6**,**8** and **9** in $CHCl_3$ solution (287 K).

## *2.3. Crystal structure description*

The X-ray studies reveal that the complexes **5-8** crystallize with one molecule per asymmetric unit cell, whereas **9** contains two independent molecules in asymmetric unit. The crystal structures of all complexes (expect for **6**) include non-coordinated solvent molecules ($CH_2Cl_2$ or hexane). Since the complexes **5**, **6**, **8** and **9** have quite similar structures, the perspective views of only molecular structures **5** and **7** are shown in Figs. 2 and 3 (structures **6**, **8** and **9** are depicted in Figs. S1-3 in ESI). Crystallographic data and the details of the structure determinations are summarized in Table 1. The selected bond lengths [Å] and bond angles [°] are given in Table 2.

Within **5-9**, the ligands are coordinated to Cu(I) through $N^1$(Py), $N^2$(Py) and $N^3$(Py) atoms thus adopting $\kappa^3$-$N,N',N''$-tripodal mode. The halogen atom completes the coordination sphere of Cu atom. To attribute the coordination geometry of latter, we have used a new four-coordinate geometry index $\tau_4$ [19], which can be calculated by Eq. (1), where α and β are the two largest bond angles around the metal.

$$\tau_4 = \frac{360-(\alpha+\beta)}{141} \qquad (1)$$

According to this criterion, for perfect tetrahedral, trigonal pyramidal or square planar geometries, the $\tau_4$ values are 1, 0.85 or 0, correspondingly [19]. The $\tau_4$ parameters calculated for complexes **5-9** [0.78, 0.81, 0.80, 0.82 and 0.84/0.78, respectively] indicate that the Cu atoms have a distorted trigonal pyramidal geometry. The $[Cu(N\text{–}C)_3P{=}X]$ cage is pseudo-$C_3$-symmetrical; the dihedral angles between three mean P–C–N–Cu blades are nearly equal and vary from 117.68 to 122.37° (the structures **6** and **8** are least symmetrical). However, the overall [Cu(L)Hal] structures are far from symmetrical since the halogen atoms are out from the pseudo-$C_3$-axes passing through P and Cu atoms (mean P–Cu–Hal = 173.5°). Within $CuN_3Hal$ coordination units, the Cu–N bonds are approximately equal in length (*ca.* 2.05 Å) and are normal relative to those in the corresponding Cu(I)-pyridine scorpionates [20]. Three N–Cu–N bit angles in each complex are also approximately equal (mean N–Cu–N = 96.02°). Phosphorus atoms expectedly exhibit a slightly distorted tetrahedral geometry ($\tau_4$ = 0.93–0.95). The P=O, P=S and P=Se bonds are fairly identical in lengths as compared to those in the free ligands {1.4792(11) [21], 1.9428(8) and 2.1050(15) Å [18], correspondingly}.

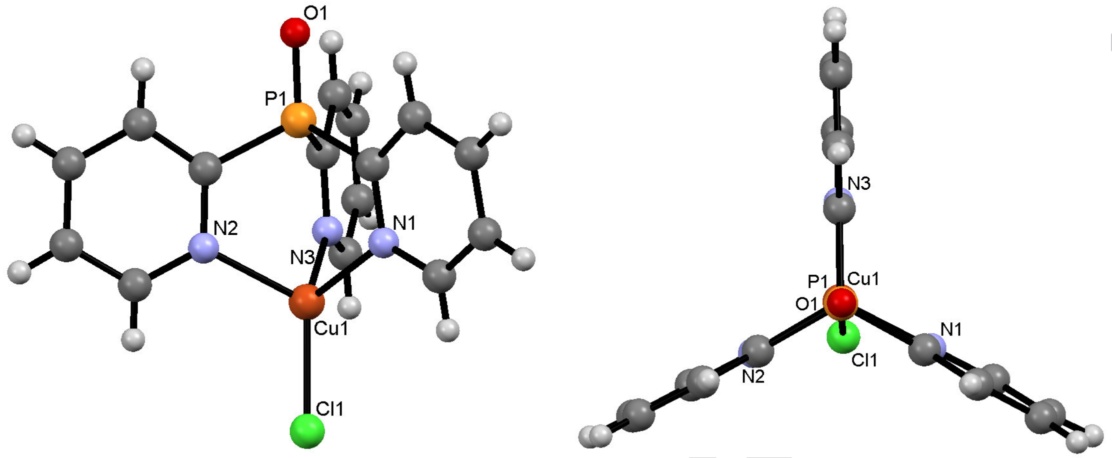


**Fig. 2.** Side-on (*left*) and top-down views of molecular structure **5** (a solvate $CH_2Cl_2$ molecule is not shown).

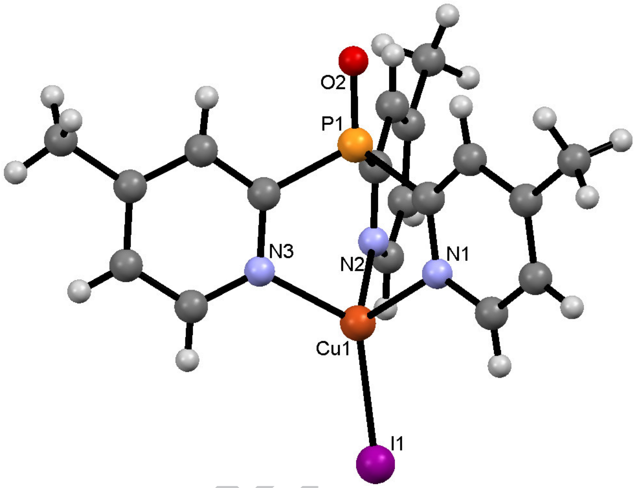


**Fig. 3.** Perspective view of molecular structure **7** (a solvate hexane molecule with partial occupancy is not shown).

As expected, the crystal structure of **10** is ionic. Due to the presence of "$PPh_3$" unit, having a propeller-type structure, the complex **10** reveals a propeller (helical) chirality. For this reason, the unit cell of **10** contains two independent cations, i.e. (*P*)- and (*M*)-helical forms (racemic mixture), and two non-coordinated $PF_6^-$ anions along with four $CHCl_3$ solvate molecules. Although the independent cations should be mirror images of each other (Figure S4), their structural metrics are different (See Table 2). The structure of one independent cation is depicted in Figure 4. Within the cation, tris(2-pyridyl)phosphine oxide behaves as a *N*,*N'*,*N''*-tridentate ligand coordinated to metal ion through three pyridine nitrogen atoms; a phosphorus atom of $PPh_3$ completes the coordination sphere of Cu(I). The latter, as follows from calculated $\tau_4$ value (0.79 and 0.78, for two independent cations), can be better described as a distorted trigonal pyramidal. Conversely, according to $\tau_4$ values (0.92 and 0.91) the geometry around phosphorus atoms of $PPh_3$ units within **10** is close to tetrahedral. The Cu–N distances vary from 2.068(8) to 2.091(7) Å and are in accordance with these values in the complexes **5-9**. Similarly, Cu–P bond lengths (*ca.* 2.18 Å) are comparable with those in the related phosphine/scorpionate complexes [22]. The P–O distances [1.468(7) and 1.476(7) Å] concur with 1.479 Å in the free ligand [21].

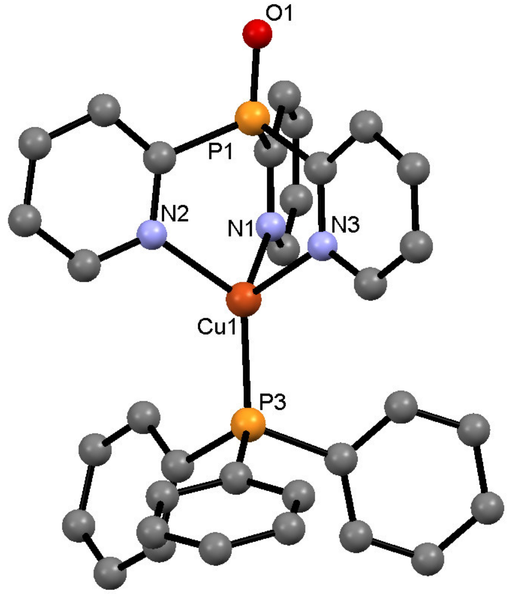


**Fig. 4.** Perspective view of a crystallographically independent cation in **10** (the hydrogen atoms are not shown).

Table 1. X-Ray crystallographic data for **5-10**.

| Compound | **5** | **6** | **7** | **8** | **9** | **10** |
|---|---|---|---|---|---|---|
| Empirical formula | $2(C_{15}H_{12}ClCuN_3OP)\cdot CH_2Cl_2$ | $C_{15}H_{12}CuIN_3OP$ | $C_{18}H_{28}CuIN_3OP\cdot 0.25(C_6H_{14})$ | $C_{15}H_{15}CuIN_3PS\cdot CH_2Cl_2$ | $3(C_{15}H_{12}CuIN_3PSe)\cdot 0.4(C_2H_4Cl_4)\cdot CH_2Cl_2$ | $[C_{33}H_{27}CuN_3OP_2]PF_6\cdot 2CHCl_3$ |
| Formula mass [g/mol] | 845.40 | 471.69 | 535.31 | 572.67 | 1756.80 | 990.76 |
| Space group | C2/c | P-1 | P-1 | P21/c | Pnma | $P2_1/n$ |
| $a$ [Å] | 23.7740(11) | 8.3028(8) | 8.6851(19) | 12.0364(8) | 17.3147(11) | 23.714(2) |
| $b$ [Å] | 8.4635(4) | 8.3462(8) | 11.634(2) | 20.1461(13) | 23.6059(17) | 15.3031(11) |
| $c$ [Å] | 17.8771(9) | 13.2733(12) | 12.233(3) | 8.3719(5) | 14.2364(9) | 23.7229(19) |
| $\alpha$ [°] | 90.00 | 73.234(3) | 87.112(7) | 90.00 | 90.00 | 90.00 |
| $\beta$ [°] | 109.783(2) | 89.578(3) | 77.891(7) | 99.6950(10) | 90.00 | 93.660(2) |
| $\gamma$ [°] | 90.00 | 65.524(3) | 70.659(7) | 90.00 | 90.00 | 90.00 |
| $V$ [Å$^3$] | 3384.8(3) | 794.89(13) | 1140.1(4) | 2001.1(2) | 5818.8(7) | 8591.3(12) |
| $Z$ | 4 | 2 | 2 | 4 | 4 | 8 |
| $D_{calcd.}$ [g·cm$^{-3}$] | 1.659 | 1.971 | 1.559 | 1.901 | 2.005 | 1.532 |
| $\mu$ [mm$^{-1}$] | 1.707 | 3.420 | 2.394 | 3.090 | 4.844 | 1.052 |
| Temperature [K] | 100(2) | 100(2) | 296(2) | 100(2) | 296(2) | 296(2) |
| Reflections collected | 48392 | 38355 | 60051 | 44913 | 87721 | 253170 |
| Independent reflections | 4088<br>[$R_{int}$ = 0.0358] | 3827<br>[$R_{int}$ = 0.0543] | 6711<br>[$R_{int}$ = 0.1565] | 4826<br>[$R_{int}$ = 0.0400] | 7194<br>[$R_{int}$ = 0.0447] | 18734<br>[$R_{int}$ = 0.1054] |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0271, 0.0698 | 0.0213, 0.0507 | 0.0449, 0.1202 | 0.0200, 0.0530 | 0.0300, 0.0695 | 0.1183, 0.3221 |
| $R_1$, $wR_2$ (all data) | 0.0296, 0.0713 | 0.0262, 0.0526 | 0.1036, 0.1304 | 0.0213, 0.0536 | 0.0377, 0.0741 | 0.1729, 0.3561 |
| Goodness of fit | 1.102 | 1.068 | 1.034 | 1.214 | 0.970 | 1.078 |

Table 2. Selected bond distances (Å) and angles (°) for complexes **5-10**.

| **Compound 5** | | | | **Compound 6** | | | |
|---|---|---|---|---|---|---|---|
| | | N(2)-Cu(1)-N(1) | 97.95(5) | | | N(2)-Cu(1)-N(1) | 94.12(7) |
| Cu(1)-N(1) | 2.0891(13) | N(3)-Cu(1)-N(1) | 95.08(5) | Cu(1)-N(1) | 2.0616(18) | N(3)-Cu(1)-N(1) | 96.60(7) |
| Cu(1)-N(2) | 2.0623(14) | N(3)-Cu(1)-N(2) | 96.26(5) | Cu(1)-N(2) | 2.0457(18) | N(3)-Cu(1)-N(2) | 97.36(7) |
| Cu(1)-N(3) | 2.0297(14) | N(1)-Cu(1)-Cl(1) | 110.95(4) | Cu(1)-N(3) | 2.0662(18) | N(1)-Cu(1)-I(1) | 122.09(5) |
| Cu(1)-Cl(1) | 2.2267(4) | N(2)-Cu(1)-Cl(1) | 112.75(4) | Cu(1)-I(1) | 2.4825(4) | N(2)-Cu(1)-I(1) | 123.50(5) |
| P(1)-O(1) | 1.4874(11) | N(3)-Cu(1)-Cl(1) | 136.76(4) | P(1)-O(1) | 1.4825(16) | N(3)-Cu(1)-I(1) | 117.05(5) |
| | | P(1)-Cu(1)-Cl(1) | 163.06 | | | P(1)-Cu(1)-I(1) | 175.55 |

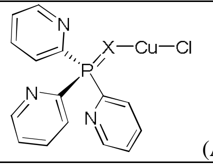
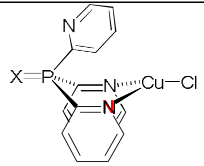
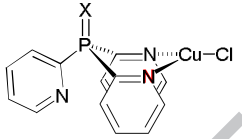
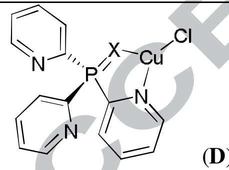
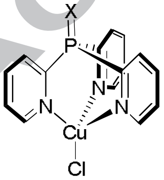
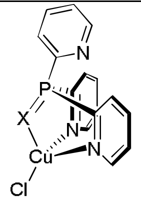
| **Compound 7** | | | | **Compound 8** | | | |
|---|---|---|---|---|---|---|---|
| | | N(2)-Cu(1)-N(1) | 95.34(12) | | | N(2)-Cu(1)-N(1) | 95.43(6) |
| Cu(1)-N(1) | 2.074(3) | N(3)-Cu(1)-N(1) | 96.97(12) | Cu(1)-N(1) | 2.0427(15) | N(1)-Cu(1)-N(3) | 98.23(6) |
| Cu(1)-N(2) | 2.060(3) | N(3)-Cu(1)-N(2) | 95.05(12) | Cu(1)-N(2) | 2.0567(15) | N(3)-Cu(1)-N(2) | 94.04(6) |
| Cu(1)-N(3) | 2.065(3) | N(1)-Cu(1)-I(1) | 115.49(9) | Cu(1)-N(3) | 2.0474(15) | N(1)-Cu(1)-I(1) | 119.06(4) |
| Cu(1)-I(1) | 2.4828(7) | N(2)-Cu(1)-I(1) | 121.49(9) | Cu(1)-I(1) | 2.4867(3) | N(2)-Cu(1)-I(1) | 121.95(4) |
| P(1)-O(1) | 1.472(3) | N(3)-Cu(1)-I(1) | 125.93(9) | P(1)-S(1) | 1.9406(6) | N(3)-Cu(1)-I(1) | 121.91(4) |
| | | P(1)-Cu(1)-I(1) | 173.57 | | | P(1)-Cu(1)-I(1) | 179.14 |

| **Compound 9** | | | | **Compound 10** | | | |
|---|---|---|---|---|---|---|---|
| | | N(1)-Cu(1)-N(8) | 96.43(12) | | | N(2)-Cu(1)-N(1) | 96.1(3) |
| | | N(1)-Cu(1)-N(81) | 96.43(12) | | | N(2)-Cu(1)-N(3) | 92.9(3) |
| Cu(1)-N(1) | 2.020(4) | N(8)-Cu(1)-N(81) | 95.41(19) | Cu(1)-N(1) | 2.091(7) | N(3)-Cu(1)-N(1) | 93.2(3) |
| Cu(1)-N(8) | 2.030(3) | N(4)-Cu(4)-N(3) | 95.79(11) | Cu(1)-N(2) | 2.071(7) | N(6)-Cu(2)-N(4) | 94.8(3) |
| Cu(1)-N(81) | 2.030(3) | N(4)-Cu(4)-N(5) | 95.17(11) | Cu(1)-N(3) | 2.086(7) | N(6)-Cu(2)-N(5) | 94.2(3) |
| Cu(4)-N(3) | 2.066(3) | N(5)-Cu(4)-N(3) | 96.79(11) | Cu(2)-N(4) | 2.083(8) | N(4)-Cu(2)-N(5) | 94.5(3) |
| Cu(4)-N(4) | 2.032(3) | N(1)-Cu(1)-I(1) | 121.54(11) | Cu(2)-N(5) | 2.085(7) | N(1)-Cu(1)-P(3) | 120.9(2) |
| Cu(4)-N(5) | 2.055(3) | N(8)-Cu(1)-I(1) | 120.46(9) | Cu(2)-N(6) | 2.068(8) | N(2)-Cu(1)- P(3) | 127.0(2) |
| Cu(1)-I(1) | 2.4760(6) | N(81)-Cu(1)-I(1) | 120.46(9) | Cu(1)-P(3) | 2.184(2) | N(3)-Cu(1)-P(3) | 118.8(2) |
| Cu(4)-I(2) | 2.4879(5) | N(3)-Cu(4)-I(2) | 111.74(8) | Cu(2)-P(4) | 2.182(2) | N(6)-Cu(2)-P(4) | 124.5(2) |
| P(1)-Se(2) | 2.0923(9) | N(4)-Cu(4)-I(2) | 124.67(8) | P(1)-O(1) | 1.468(7) | N(4)-Cu(2)-P(4) | 116.0(2) |
| P(3)-Se(1) | 2.0976(12) | N(5)-Cu(4)-I(2) | 125.88(8) | P(2)-O(2) | 1.476(7) | N(5)-Cu(2)-P(4) | 125.2(2) |
| | | P(1)-Cu(4)-I(2) | 170.60 | | | P(1)-Cu(1)-P(3) | 175.22 |
| | | P(3)-Cu(1)-I(1) | 179.07 | | | P(2)-Cu(2)-P(4) | 173.81 |

### *2.4. DFT computations*

To explain the observed selectivity in complexation of TPPCs with copper(I) halides, we have performed DFT computation for model 1:1 complexes of CuCl with ligands **1**, **3** and **4** at B3LYP/6-311+G(d,p) level both for isolated states and for $CHCl_3$ solution (ε = 4.8). The computations predict that five (for $Py_3P{=}O$) and six (for $Py_3P{=}S$ and $Py_3P{=}Se$) different isomers are possible, in which metal is di-, three- and four-coordinated by nitrogen and/or chalcogen atoms of ligand in a linear, trigonal planar or tetrahedral arrangement. The optimized geometries of all the complexes are given in ESI and their relative free Gibbs energies are listed in Table 3. For complex [Cu(2-$Py_3P{=}O$)Cl] (**5**), the computed geometry is in reasonable agreement with the experimental one; the inevitable disagreements are caused by packing effects and intermolecular interactions within crystals. From the Table 1, it can be seen that the scorpionate isomers **E** are most stable both for isolated states and for solution. The decrease in energy at the formation of **E** type complexes from CuCl and ligands **1**, **3** and **4** is 48.8, 46.9 и 46.5 kcal/mol, correspondingly.

**Table 3.** The relative free energies (kcal/mol) of isomeric TPPC complexes with CuCl for isolated states and $CHCl_3$ solution (in brackets) from B3LYP/6-311+G(d,p) computations.

| Structure | X | | |
|---|---|---|---|
| | O | S | Se |
|  (**A**) | 6.54<br>(10.47) | 4.89<br>(9.46) | 4.17<br>(7.18) |
|  (**B**) | 4.09<br>(8.53) | 3.75<br>(2.20) | 3.80<br>(2.51) |
|  (**C**) | 9.75<br>(9.54) | 8.18<br>(11.19) | 8.10<br>(10.10) |
|  (**D**) | 6.48<br>(4.08) | 5.48<br>(3.38) | 5.20<br>(2.27) |
|  (**E**) | 0.00<br>(0.00) | 0.00<br>(0.00) | 0.00<br>(0.00) |
|  (**F**) | – | 8.53<br>(5.48) | 7.79<br>(6.57) |

## 3. Conclusions

To summarize, complexation of tris(2-pyridyl)phosphine chalcogenides with copper(I) halides occurs selectively to afford earlier unknown scorpionate complexes, [Cu(*N*,*N'*,*N''*-2-$Py_3P{=}X$)Hal] (X = O, S and Se), in which Cu(I) ion, coordinated by three pyridine nitrogen atoms of the ligand and halogen atom, adopts approximately trigonal pyramidal geometry. According to DFT calculations, the realized *N*,*N'*,*N''*-coordination of the ligands toward Cu ion is thermodynamically more preferable (both for isolated states and for solution) among all the possible coordinating patterns. The synthesized scorpionates are prospective anticancer drugs [23] and catalysts [24] as well as models for the binding sites of copper proteins [25]. Moreover, the phosphine/scorpionate complex **10** is close analogue of known anticancer [26] and antiproliferative active compounds [27].

## 4. Experimental

### *4.1. General*

All reactions were performed under argon atmosphere. The ligands **1**-**4** were synthesized by oxidation of tris(2-pyridyl)- and tris(4-methyl-2-pyridyl)phosphines with $H_2O_2$, powdered sulfur ($S_8$) or selenium [18]. The initial phosphines were prepared from red phosphorus and 2-bromopyridines according to published method [2]. All remaining chemicals were purchased and used as received. The $^1H$ and $^{31}P$ NMR spectra were recorded on a Bruker AV-400 spectrometer at 400.13 and 161.98 MHz, respectively. The $^1H$ NMR chemical shifts are expressed with respect to residual protonated $CDCl_3$ (7.27 ppm). $^{31}P$ NMR spectra were referenced externally against 85% $H_3PO_4$ (δ = 0 ppm). UV-Vis spectra were measured on a Lambda 35 spectrophotometer at ambient temperature ($CHCl_3$, d = 0.1-0.3 cm). Elemental analysis was performed using a Flash EA 1112 analyzer. Melting points were determined with a Kofler micro hot stage.

### *4.2. Synthesis of complexes **5**-**9** (general procedure)*

To a solution of the ligand **1**-**4** (0.12 mmol) in $CH_2Cl_2$ (5 mL), CuCl or CuI (0.12 mmol) was added. The suspension was stirred at ambient temperature for 10 min and then filtered. Hexane (7 mL) was carefully added to a filtrate so that the latter was covered by hexane layer. After 15-30 hours, X-ray quality crystals of **5**-**9** were precipitated. The crystals were filtered, washed with hexane–$CH_2Cl_2$ mixture (9:1) and dried on air.

### *4.3. Synthesis of complex **10***

To a solution of ligand **1** (28 mg, 0.10 mmol) in $CHCl_3$ (7 mL), $[Cu(MeCN)_4]PF_6$ (37 mg, 0.10 mmol) was added. The mixture was stirred at ambient temperature for 1-2 min to give a clear orange solution. To latter, $Ph_3P$ (26 mg, 0.10 mmol) was added; the mixture was stirred until homogenization and then filtered. Hexane (7 mL) was carefully added to a filtrate so that the latter was covered by hexane layer. The precipitated crystals of **10** were retrieved, washed with hexane–$CHCl_3$ mixture (6:4) and dried on air.

### *4.4. Synthesis of complex [Cu(2-$Py_3P{=}O$)($AsPh_3$)]$PF_6$ (**11**)*

To a solution of **1** (28 mg, 0.10 mmol) and $[Cu(MeCN)_4]PF_6$ (37 mg, 0.10 mmol) in $CHCl_3$ (7 mL), $Ph_3As$ (26 mg, 0.10 mmol) was added. The mixture was stirred at ambient temperature for 1-2 min to give a clear yellow solution. The latter was evaporated in vacuum and the residue was triturated in diethyl ether (10 mL). The powder obtained was dried in vacuum (1 bar) to give **11** as yellowish powder. Our attempts to growing X-ray quality crystals of **11** from usual solvent systems were unsuccessful.

### *4.5. Characterization data for complexes **5-11***

*[Cu(2-Py$_3$P=O)Cl]·0.5CH$_2$Cl$_2$ (**5**).* Garnet crystals, > 150 °C dec. Yield: 45 mg (88%). $^1$H NMR (400.13 MHz, CDCl$_3$, ppm), $\delta$: 5.31 (s, 2H, CH$_2$Cl$_2$), 7.53 (t, $^3J_{HH}$ = 6.5 Hz, 3H, Py), 7.94-7.99 (m, 3H, Py), 8.40 (t, $^3J_{HH}$ = 7.0 Hz, 3H, Py), 9.03 (d, $^4J_{PH}$ = 4.7 Hz, 3H, Py). $^{31}$P NMR (161.98 MHz, CDCl$_3$, ppm), $\delta$: –9.45. UV-Vis (CHCl$_3$, $\lambda_{max}$/nm): 259, 342, 447. Anal. Calcd for $C_{15}H_{12}ClCuN_3OP·0.5CH_2Cl_2$ (422.71): C, 44.04; H, 3.10; N, 9.94. Found: C, 43.75; H, 3.01; N, 10.17.

*[Cu(2-Py$_3$P=O)I] (**6**).* Garnet crystals, stable up to 200 °C. Yield: 41 mg (72%). $^1$H NMR (400.13 MHz, CDCl$_3$, ppm), $\delta$: 5.52-5.56 (m, 3H, Py), 7.94-8.00 (m, 3H, Py), 8.38-8.42 (m, 3H, Py), 9.05-9.06 (m, 3H, Py). $^{31}$P NMR (161.98 MHz, CDCl$_3$, ppm), $\delta$: –7.75. UV-Vis (CHCl$_3$, $\lambda_{max}$/nm): 257, 333, 430. Anal. Calcd for $C_{15}H_{12}CuIN_3OP$ (471.70): C, 38.19; H, 2.56; N, 2.56. Found: C, 38.10; H, 2.68; N, 2.41.

*{Cu[(4-Me-2-Py)$_3$P=O]I}·0.25C$_6$H$_{14}$ (**7**).* Garnet crystals, stable up to 200 °C. Yield: 43 mg (67%). $^1$H NMR (400.13 MHz, CDCl$_3$, ppm), $\delta$: 0.88-0.91 (t, $^3J_{HH}$ = 7.0 Hz, 6H, *Me*CH$_2$), 1.24-1.33 (m, 8H, *CH$_2$*Me), 2.42 (s, 9H, *Me*Py), 7.30 (d, $^3J_{PH}$ = 4.4 Hz, 3H, Py), 8.20 (d, $^3J_{HH}$ = 7.1 Hz, 3H, Py), 8.87 (d, $^4J_{PH}$ = 5.0 Hz, 3H, Py). $^{31}$P NMR (161.98 MHz, CDCl$_3$, ppm), $\delta$: –6.64. Anal. Calcd for $C_{24}H_{32}CuIN_3OP·0.25C_6H_{14}$ (535.31): C, 43.75; H, 4.05; N, 7.85. Found: C, 44.21; H, 4.12; N, 7.64.

*[Cu(2-Py$_3$P=S)I]·CH$_2$Cl$_2$ (**8**).* Garnet crystals, stable up to 200 °C. Yield: 51 mg (75%). $^1$H NMR (400.13 MHz, CDCl$_3$, ppm), $\delta$: 5.31 (s, 2H, CH$_2$Cl$_2$), 5.51-5.54 (m, 3H, Py), 7.94-7.97 (m, 3H, Py), 8.76 (t, $^3J_{HH}$ = 8.0 Hz, 3H, Py), 9.07 (d, $^4J_{PH}$ = 4.5 Hz, 3H, Py). $^{31}$P NMR (161.98 MHz, CDCl$_3$, ppm), $\delta$: 11.82. UV-Vis (CHCl$_3$, $\lambda_{max}$/nm): 260, 335, 444. Anal. Calcd for $C_{16}H_{14}Cl_2CuIN_3PS$ (572.70): C, 33.56; H, 2.46; N, 7.34. Found: C, 33.42; H, 2.58; N, 7.21.

*[Cu(2-Py$_3$P=Se)I]·0.6CH$_2$Cl$_2$ (**9**).* Garnet crystals, > 165 °C dec. Yield: 49 mg (70%). $^1$H NMR (400.13 MHz, CDCl$_3$, ppm), $\delta$: 5.31 (s, 2H, CH$_2$Cl$_2$), 5.50-5.54 (m, 3H, Py), 7.94-7.99 (m, 3H, Py), 8.91 (t, $^3J_{HH}$ = 8.5 Hz, 3H, Py), 9.06 (d, $^4J_{PH}$ = 4.8 Hz, 3H, Py). $^{31}$P NMR (161.98 MHz, CDCl$_3$, ppm), $\delta$: 10.29. UV-Vis (CHCl$_3$, $\lambda_{max}$/nm): 259, 326, 444. Anal. Calcd for $C_{15}H_{12}CuIN_3PSe·0.6CH_2Cl_2$ (586.62): C, 31.99; H, 2.27; N, 7.18. Found: C, 31.71; H, 2.12; N, 7.59.

*[Cu(2-Py$_3$P=O)(PPh$_3$)]PF$_6$·2CHCl$_3$ (**10**).* Yellowish crystals, mp 134-136 °C. Yield: 88 mg (89%). $^1$H NMR (400.13 MHz, CDCl$_3$, ppm), $\delta$: 7.49-7.59 (m, 18H, Ph, Py), 8.12-8.16 (m, 3H, Py), 8.25 (d, $^4J_{PH}$ = 4.7 Hz, 3H, Py), 8.55 (t, $^3J_{HH}$ = 7.0 Hz, 3H, Py). $^{31}$P NMR (161.98 MHz, CDCl$_3$, ppm), $\delta$: –8.30 and –8.22 (s, Py$_3$P=O, Ph$_3$P), –143.78 (quint, $^1J_{PF}$ = 716 Hz, PF$_6$). Anal. Calcd for $C_{35}H_{29}Cl_6CuF_6N_3OP_3$ (990.80): C, 42.43; H, 2.95; N, 4.24. Found: C, 42.30; H, 2.71; N, 4.10.

*[Cu(2-Py$_3$P=O)(AsPh$_3$)]PF$_6$ (**11**).* Yellowish powder, > 252 °C dec. Yield: 68 mg (85%). $^1$H NMR (400.13 MHz, CDCl$_3$, ppm), $\delta$: 7.47-7.58 (m, 18H, Ph, Py), 8.12-8.17 (m, 3H, Py), 8.35 (d, $^4J_{PH}$ = 4.5 Hz, 3H, Py), 8.54 (t, $^3J_{HH}$ = 7.2 Hz, 3H, Py). $^{31}$P NMR (161.98 MHz, CDCl$_3$, ppm), $\delta$: –8.82 (s, Py$_3$P=O), –144.03 (quint, $^1J_{PF}$ = 712 Hz, PF$_6$). Anal. Calcd for $C_{33}H_{27}AsCuF_6N_3OP_2$ (795.99): C, 49.79; H, 3.42; N, 5.28. Found: C, 49.50; H, 3.25; N, 5.50.

### *4.6. X-ray crystallography*

Data were collected on a Bruker D8 Venture diffractometer with MoK$_\alpha$ ($\lambda$ = 0.71073 Å) radiation using the $\varphi$ and $\omega$ scans. An empirical absorption correction was applied using the SADABS program [28]. The structures were solved and refined by direct methods using the SHELX [29]. All non-hydrogen atoms were refined anisotropically using SHELX [29]. The coordinates of the hydrogen atoms were calculated from geometrical positions (except for **9**, the mixed method was used). Within **7**, the hexane molecule is disordered over two sites, each in 50% occupancy (refined isotropically). Within **9**, the C(1A)Cl(1A)Cl(2A) molecule is disordered over two sites at 50:50 probability.

### *4.7. Computational details*

All the computations were performed with the Gaussian 09 package [30]. The equilibrium geometries were calculated using B3LYP functional [31] and 6-311+G(d,p) basis set. Frequency calculations at the same level of theory were also performed to identify all the stationary points as minima (zero imaginary frequencies). To estimate the effect of solvent medium (CHCl$_3$, $\varepsilon$ = 4.8) on the energetics of obtained structures, the self-consistent reaction field (SCRF) approach based on the polarized continuum model (IPCM) [32] was used at the same level of theory to calculate the single-point energy with solvent for the gas phase stationary points.

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## Appendix A. Supplementary material

CCDC 1010958-1010962 (**5-9**) 1019410 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem… .

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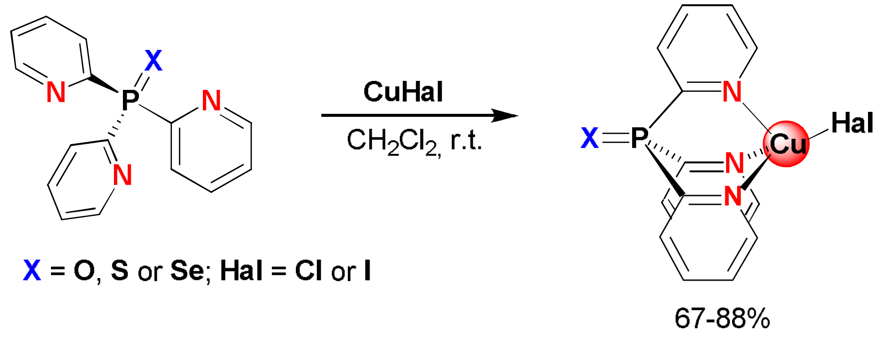
## Graphical abstract



## Graphical abstract (Synopsis)

Tris(2-pyridyl)phosphine chalcogenides selectively coordinate copper(I) halides *via* three pyridyl nitrogen atoms to afford earlier unknown Cu(I) scorpionates, [Cu($N$,$N'$,$N''$-2-$Py_3P{=}X$)Hal] (X = O, S and Se), in 67-88% yield. The latter have been characterized by X-ray crystallography, NMR and UV-Vis spectroscopy.