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Copper(I) and silver(I) tertiary phosphines complexes: Synthesis, X-ray structures and spectroscopic characterization

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Six new complexes, $[Cu_4I_4(PPh_2Cy)_4]\cdot 2H_2O$ (**1**), $[CuI(PPhCy_2)_2]$ (**2**), $[CuCl(PPhCy_2)_2]$ (**3**), and $[CuBr(PPh_3)_3]\cdot CH_3CN$ (**4**), $[Ag(PPhCy_2)_2(NO_3)]$ (**5**), $[Ag(PCy_3)(NO_3)]_2$ (**6**) [where Ph = phenyl, Cy = cyclohexyl], have been synthesized and structurally characterized by X-ray diffraction, IR absorption spectra and NMR spectroscopic studies (except complex **4**). The X-ray diffraction analysis of complex (**1**), pseudo polymorph of complex $[Cu_4I_4(PPh_2Cy)_4]$, reveals a stella quadrangula structure. The four corners of the cube are occupied by copper(I) atoms and four I atoms are present at the alternative corners of the cube, further more the copper(I) atoms are coordinated to a monodentate tertiary phosphine. Complexes (**2**) and (**3**) are isostructural with trigonal planar geometry around the copper(I) atom. The crystal structure of complex (**4**) is a pseudo polymorph of complex $[CuBr(PPh_3)_3]$ and the geometrical environment around the copper(I) centre is distorted tetrahedral. In the Ag^I complexes (**5**) and (**6**), the central metal atoms have pseudo tetrahedral and trigonal planar geometry, respectively. Spectroscopic and microanalysis results are consistent with the single crystal X-ray diffraction studies.

1. Introduction

Our interest in the Cu^I and Ag^I compounds with monodentate tertiary phosphine ligands; is to explore the structural chemistry of these complexes and their mixed ligand multi-dimensional complexes of versatile architectures. Reaction of coin metal(I) salts with monodentate tertiary phosphine bases yielded an array of two, three, and four coordinated complexes with diverse structural properties that are determined by the specific choice of the phosphine ligand and to a lesser extent, by the choice of counter ions [1]. Neutral phosphine and amine ligands form mono- or multi-nuclear complexes with copper(I) and copper(II) salts, in which the coordination number ranges from two to four [2–10]. The greatest range of structural types has been found for the case of tertiary phosphines, of which the most extensively studied is triphenyl phosphine and to a lesser extent tricyclohexyl phosphine [11–16].

The geometry around the copper(I) atom in complexes with tertiary phosphine ligands depends on the stoichiometric ratio of the metal salt and ligand used, as well as the solvent of crystallization. Thus for a compound of 1:1 stoichiometry monomer, dimer and tetramer complexes are possible with general formulae of $[MX(PR_3)]$, $[M_2X_2(PR_3)_2]$ and $[M_4X_4(PR_3)_4]$ (where M = Ag and Cu. R = phenyl, alkyl, aryl or cyclohexyl groups) [1,17–20]. Whereas, the compounds with stoichiometry 1:1.5 are dimers [15,16], and compounds with stoichiometry 1:2 and 1:3 are monomers and dimers with tetrahedral and trigonal planar geometries, respectively, around the metal centre [11,22–24]. The complexes of general formula $[M_4X_4(PR_3)_4]$ (X = Cl, Br or I) have pseudo cubane-like structures [10,25,26]. These types of structures can be described as two interpenetrating tetrahedra of four metals (M) and four triply bridging halides (anions) situated on alternative corners of a distorted cube with each metal atom being further coordinated to one terminal monodentate ligand [17]. Frequently a non-systematic deviation of the cubane core from the idealized tetrahedral geometry is observed for cubane-like metal clusters [27–29].

Tertiary phosphine complexes of silver(I) of the type $[AgXL_n]$, where L = tertiary phosphine; $n = 1–4$; X = coordinating or non-coordinating anion, were first prepared as early as 1937 [30–38]. The reaction of silver(I) salts with monodentate tertiary phosphines in a 1:2 stoichiometric ratio generally results in the formation of either monomeric $[AgX(PR_3)_2]/[Ag(PR_3)_2]\cdot X$ [39–51], or dimeric complexes $[AgX(PR_3)_2]_2$ [51–54], depending on the donor properties of the phosphine ligand, the bulkiness of this ligand, and the donor properties of the anion. These complexes show a diversity of structural types and several reviews on this topic have been published [31–38]. The metal centre in the majority of the neutral $[AgX(PR_3)_2]$ and $[AgX(PR_3)_2]_2$ complexes are predominantly four coordinate, with the anion acting as either a bi-dentate chelating ligand or as a bridging ligand. Two or three coordination have been found only in circumstances where the anion is a weak donor or the substituents on the phosphine ligand are bulky [43,46–51].

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Although a large number of copper(I) complexes with monodentate tertiary phosphine have been reported [1,11–15], such complexes with neutral phosphines are consider as good starting materials for the crystal synthesis of metal organic frameworks of pre-designed architectures and properties [6–8,14,55,56]. Herein, we report the synthesis and structural characterization of six metal(I) complexes with tertiary phosphines. The X-ray structures, IR absorption spectra and NMR spectral data are also described herein.

2. Experimental

2.1. Material and physical measurements

All chemical and solvents were of analytical grade (purchased from Aldrich and ACROS) and were used without further purification. Microanalysis was done by Mr. D. Mooser (Ecole d'ingénieurs de Fribourg, Filière de chimie). The IR spectra were recorded as KBr pellets on a PerkinElmer Spectrum One FTIR instrument. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AMX 400 MHz using CD_2Cl_2 as solvent. TMS was used as the internal standard. We have experienced for the synthesis of the silver(I) complexes in the presence of phosphines that a discoloration or the formation of silver particles is very slow and takes a number of weeks. Hence, these reactions were carried out under normal laboratory conditions.

2.2. Synthesis of $[Cu_4I_4(PPh_2Cy)_4].2H_2O$ (**1**)

For the synthesis of complex (**1**) CuI (0.19 g, 0.1 mmol) and PPh_2Cy (0.268 g, 0.1 mmol) were dissolved in 20 ml of CH_2Cl_2/MeOH (2:1). The reaction mixture was stirred for 10 min at room temperature. The clear solution obtained was filtered to avoid any impurity and kept at room temperature for slow evaporation. After two days colourless block crystals were obtained. A suitable crystal was chosen for X-ray diffraction analysis (Yield: 75%). *Anal.* Calc. for $C_{72}H_{88}Cu_4I_4P_4O_2$: C, 46.18; H, 4.70. Found: C, 46.07; H, 4.68%. IR (ν, cm^{-1}): 3523b, 3414m, 3051w, 2924vs, 2847s, 1618vw, 1480m, 1432vs, 1331m, 1271m, 1169m, 1000m, 887m, 742vs, 527s. ^{1}H NMR (CD_2Cl_2; ppm): 1.6–2.0, 2.5 (m, 11H, cyclohexyl protons), and 7.3–7.7 (m, 10H, phenyl protons). ^{13}C NMR (CD_2Cl_2; ppm): 26.0–36.0 (cyclohexyl carbons), and 128.2–134.0 (phenyl carbons). ^{31}P NMR (CD_2Cl_2; ppm): −9.3 (s, sharp).

2.3. Synthesis of $[CuI(PPhCy_2)_2]$ (**2**)

CuI (0.19 g, 0.1 mmol) and $PPhCy_2$ (0.55 g, 0.2 mmol) in 20 ml of MeCN were dissolved by continuous stirring with moderate heating. A small amount of $CHCl_3$ was added as solvent of crystallization. The colourless clear solution obtained was filtered to avoid any impurity and kept undisturbed for crystallization. After three days colourless plate-like crystals were obtained. A suitable crystal was chosen for X-ray diffraction studies (Yield: 67%). *Anal.* Calc. for $C_{36}H_{54}CuIP_2$: C, 58.44; H, 7.30. Found: C, 58.35; H, 7.28%. IR (ν, cm^{-1}): 3417m, 3045w, 2922vs, 2842s, 1619vw, 1483m, 1412vs, 1323m, 1275m, 1173m, 997m, 883m, 752vs, 526s. ^{1}H NMR (CD_2Cl_2; ppm): 1.2–2.4 (m, 22H, cyclohexyl protons), and 7.3–7.6 (m, 5H, phenyl protons). ^{13}C NMR (CD_2Cl_2; ppm): 26.1–32.5 (cyclohexyl carbons), and 127.9–134.7 (phenyl carbons). ^{31}P NMR (CD_2Cl_2; ppm): 6.3 (s, sharp).

2.4. Synthesis of $[CuCl(PPhCy_2)_2]$ (**3**)

$CuCl_2$ (0.135 g, 0.1 mmol) and $PPhCy_2$ (0.55 g, 0.2 mmol) were dissolved by gentle heating and continuous stirring for 20 min in 20 ml of MeOH/H_2O (3:1), 10 ml of MeCN was added to the above reaction mixture to get a transparent solution. The clear solution obtained was filtered to avoid any impurity and kept at room temperature for slow evaporation. After five days plate-like crystals were obtained. The crystalline product was collected by filtration and air dried. During this reaction Cu(II) is reduced to Cu(I) in the presence of strong reducing agents like tertiary phosphines. A suitable crystal was chosen for X-ray diffraction analysis (Yield: 78%). *Anal.* Calc. for $C_{36}H_{54}ClCuP_2$: C, 66.70; H, 8.34. Found: C, 66.62; H, 8.28%. IR (ν, cm^{-1}): 3413m, 3053w, 2929vs, 2837s, 1613vw, 1471m, 1410vs, 1343m, 1259m, 1165m, 1008m, 873m, 755vs, 499s. ^{1}H NMR (CD_2Cl_2; ppm): 1.2–2.4 (m, 22H, cyclohexyl protons), and 7.1–7.4 (m, 5H, phenyl protons). ^{13}C NMR (CD_2Cl_2; ppm): 26.2–32.4 (cyclohexyl carbons), and 127.9–134.5 (phenyl carbons). ^{31}P NMR (CD_2Cl_2; ppm): 6.3 (s, sharp).

2.5. Synthesis of $[CuBr(PPh_3)_3].CH_3CN$ (**4**)

$CuBr_2$ (0.224 g, 0.1 mmol) and PPh_3 (0.525 g, 0.2 mmol) in 15 ml CH_2Cl_2 were dissolved by continuous heating and mechanical stirring at 30 °C for 20 min. The resultant reaction mixture was further treated with thiosemicarbazide (0.091 g, 0.1 mmol) in 10 ml of MeCN/MeOH (1:1) solution. The reaction mixture was stirred for 20 min again. The resultant clear solution was filtered to avoid any impurity and kept undisturbed at room temperature for slow evaporation. During this reaction process, according to expectations, Cu(II) was reduced to Cu(I) in the presence of the strong reducing agent, triphenyl phosphine. After seven days colourless block crystals of unexpected product were obtained. A suitable crystal was chosen for X-ray diffraction analysis. (Yield: 70%). *Anal.* Calc. for $C_{56}H_{48}NBrCuP_3$: C, 69.18; H, 4.94; N, 1.44. Found: C, 69.13; H, 4.98; N, 1.47%. IR (ν, cm^{-1}): 3413m, 3049s, 2223w, 1616w, 1584m, 1478vs, 1308m, 1154s, 997m, 741vs, 693s, 507vs. No NMR spectroscopic characterization was done due to the poor solubility of the complex in the available solvents.

2.6. Synthesis of $[Ag(PPhCy_2)_2(NO_3)]$ (**5**)

To a solution of $AgNO_3$ (0.017 g, 0.1 mmol) in distilled water (5 mL) was added dicyclohexylphenyl phosphine (0.055 g, 0.2 mmol) in acetone/acetonitrile (1:1) (20 mL). The reaction mixture was stirred for 2 h at rt. The clear solution obtained was filtered and left at rt for slow evaporation. After a few days colourless plate-like crystals were obtained (Yield: 68%). *Anal.* Calc. for $C_{36}H_{54}AgNO_3P_2$: C, 60.11; H, 7.51; N, 1.95. Found: C, 60.43; H, 7.62; N, 2.28%. IR (ν, cm^{-1}): 3551m, 3478s, 3412s, 3075w, 3052w, 2928vs, 2858s, 1638m, 1617s, 1447vs, 1277m, 1175s, 1003s, 847m, 658vs, 533m. ^{1}H NMR (CD_2Cl_2-d_2; ppm): 1–2.6 (m, 22H, cyclohexyl protons), and 7–8 (m, 5H, phenyl protons). ^{13}C NMR (CD_2Cl_2-d_2; ppm): 26.1–32.8 (cyclohexyl carbons), and 128.6–135.0 (phenyl carbons). ^{31}P NMR (CD_2Cl_2-d_2; ppm): 24.1–27.1 (d. one peak for phosphorous atom of tertiary phosphine).

2.7. Synthesis of $[Ag(PCy_3)(NO_3)]_2$ (**6**)

To a solution of $AgNO_3$ (0.017 g, 0.1 mmol) in distilled water (5 mL) was added tricyclohexyl phosphine (0.028 g, 0.1 mmol) in acetone (15 mL). After the reaction mixture was stirred for 1 h at rt. The colourless solution obtained was filtered to avoid any impurity and left undisturbed for slow evaporation. After three days colourless block-like crystals were obtained (Yield: 78%). *Anal.* Calc. for $C_{36}H_{66}Ag_2N_2O_6P_2$: C, 47.96; H, 7.32; N, 3.10. Found: C, 48.67; H, 7.46; N, 3.13%. IR (ν, cm^{-1}): 3551m, 3412m, 2918s, 2828s, 1638m, 1616s, 1446vs, 1297m, 1174s, 1005s, 839vs, 557s. ^{1}H NMR (CD_2Cl_2-d_2; ppm): 1.2–2.0 (m, 22H, cyclohexyl protons). ^{13}C NMR (CD_2Cl_2-d_2; ppm): 26.2–32.3 (cyclohexyl carbons). ^{31}P NMR

(CD_2Cl_2-d_2; ppm): 42.3 (d. single peak for phosphorous atom of tricyclohexyl phosphine).

2.8. X-ray crystallography

The intensity data were collected at 173 K on either, a one circle (ϕ scans) [57], or a two circle (ω and ϕ scans) [58] Stoe Image Plate Diffraction System, using Mo Kα graphite monochromated radiation. The structures were solved by Direct methods using the program SHELXS-97 [59]. The refinement and all further calculations were carried out using SHELXL-97 [59]. The H-atoms were either located from Fourier difference maps and freely refined or included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. Empirical or multi-scan absorption corrections were applied using the REFdelABS and MULscanABS routines in [60]. For compound **1** a region of diffuse electron density was treated with the SQUEEZE routine in PLATON [60]. The electron density was estimated to be equivalent to 4 water molecules of crystallization per unit cell, or two water molecules per molecule of complex (space group $P\bar{1}$, $Z = 2$). Figs. 1–6 were drawn using the program Mercury [61]. A summary of crystal data and refinement details for compounds **1**–**6** are given in Table 1, and selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Structural descriptions

*3.1.1. [$Cu_4I_4(PPh_2Cy)_4$]·$2H_2O$ (**1**)*

The crystal structure of [$Cu_4I_4(PPh_2Cy)_4$]·$2H_2O$ (**1**) has been determined at low temperature and the molecular structure is given in Fig. 1. Selected bond lengths and angles are tabulated in Table 2. The asymmetric unit of complex **1** consists of one molecule of [$Cu_4I_4(PPh_2Cy)_4$] and two water molecules of crystallization. It is a pseudo polymorph of the non-hydrated form, [$Cu_4I_4(PPh_2Cy)_4$], which crystallized in the monoclinic space group $C2/c$ [21], compared to **1** which crystallises in the triclinic space group $P\bar{1}$ (Table 1). It is also isostructural with the molecular complexes of general formula [$Cu_4X_4(PPh_3)_4$] [27–29].

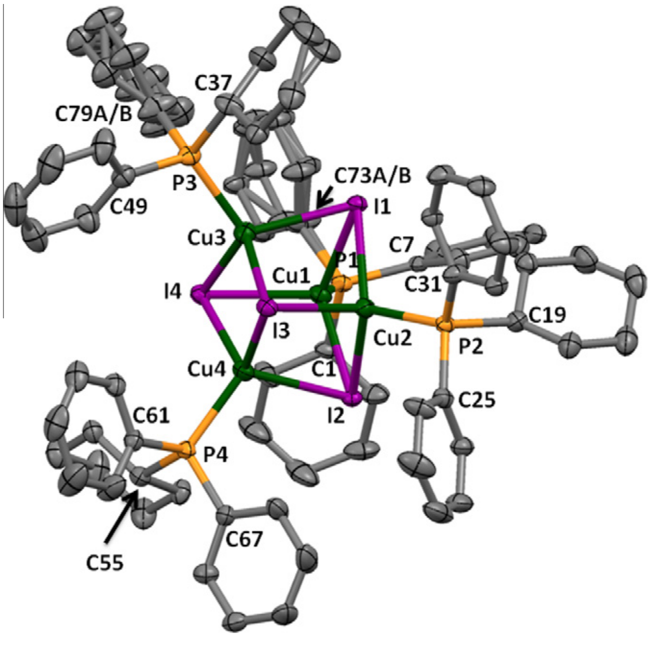

Fig. 1. View of the molecular structure of complex **1**, with selected atom labelling scheme and the displacement ellipsoids drawn at the 30% probability level [H-atoms have been omitted for clarity].

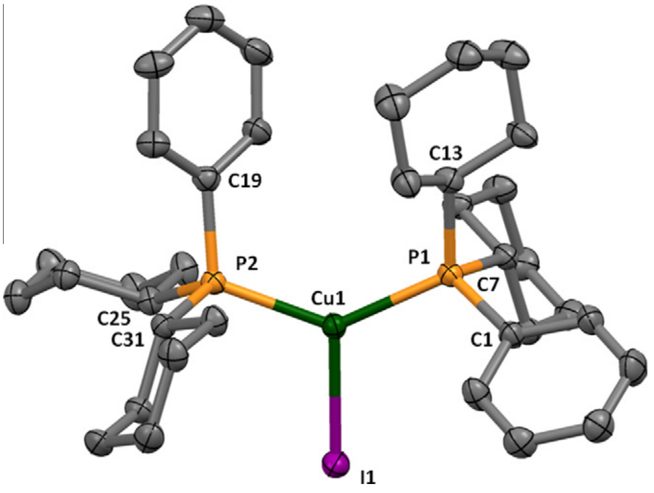

Fig. 2. View of the crystal structure of complex **2**, with a partial atom labelling scheme and the displacement ellipsoids drawn at the 30% probability level [H-atoms have been omitted for clarity].

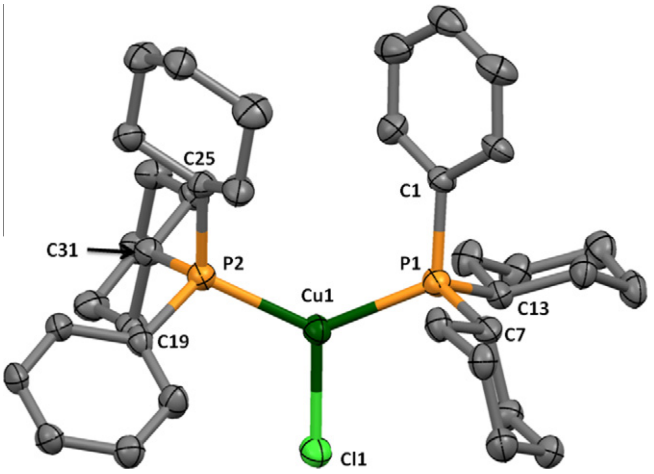

Fig. 3. View of the molecular structure of complex **3** with selected atom labelling scheme and the displacement ellipsoids drawn at the 30% probability level [H-atoms have been omitted for clarity].

The central unit of complex **1** can be described as a strongly distorted cube in which four corners are occupied by four I atoms and on alternative corners of the cube there are four Cu^I atoms, which are coordinated with a monodentate tertiary phosphine as a terminal ligand. The molecular structure of the complex adopts a cubane-like configuration with two interpenetrating tetrahedra of complex; the copper and iodine atoms form a markedly distorted cube (as shown in Fig. 1), each copper atom being further coordinated to a diphenylcyclohexyl phosphine ligand.

The most notable structural feature of complex **1** is that both the bonding and nonbonding distances of the Cu_4I_4 core deviate greatly from the idealized cubic tetrahedral geometry expected from bonding considerations. In this distorted cubane-like structure the average Cu···Cu distance is ca. 2.966 Å; the I···I interatomic distances vary from ca. 4.18 to 4.30 Å. The Cu–I distances range from 2.6402(8) to 2.7252(7) Å. These inter-cubane distances indicate that there is no metal–metal interaction (d^{10}–d^{10} interaction) in the solid state structure of **1**. Interatomic distances found in complex **1** are comparable with those in similar reported structures [10,21,27–29].

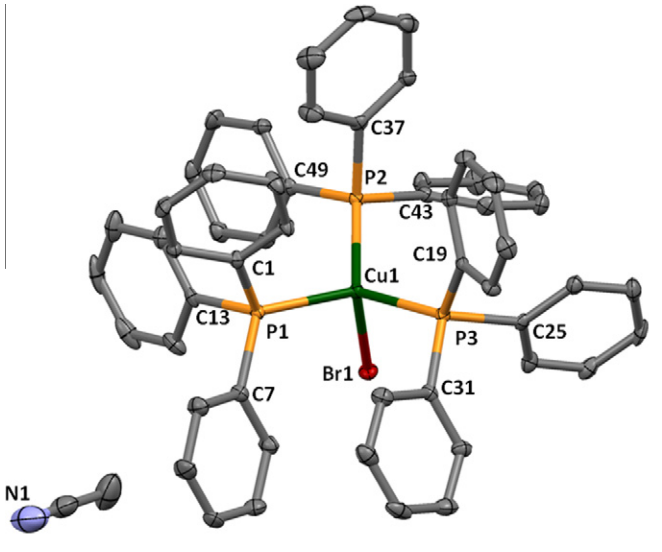

Fig. 4. A view of the molecular structure of complex **4**·$\mathbf{CH_3CN}$, with partial atom labelling and displacement ellipsoids drawn at the 30% probability level [H-atoms have been omitted for clarity].

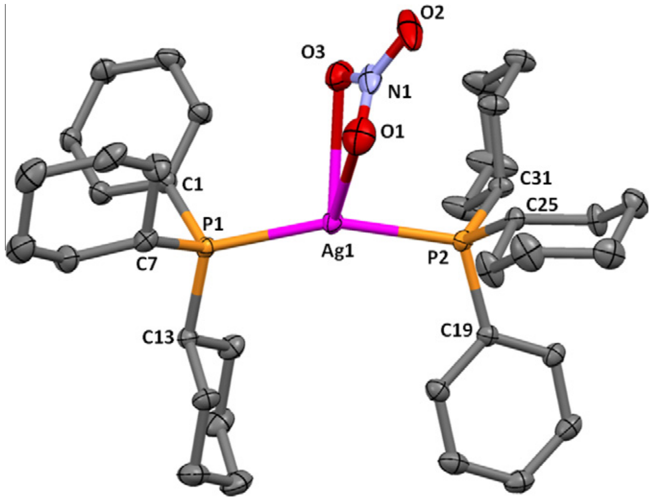

Fig. 5. A view of the molecular structure of compound **5**, with displacement ellipsoids drawn at the 30% probability level [H-atoms have been omitted for clarity].

The evidence concerning the large deformation of the Cu_4I_4 core is given by the Cu–I–Cu angles, which range from 67.19(3)° to 73.72(2)°, and the I–Cu–I angles, which vary from 100.90(2)° to 111.30(3)°. These bond angles describe well the deviation from ideal cubane-like structures.

3.1.2. *[CuI($PPhCy_2$)$_2$] (**2**)*

A perspective view of the molecular structure of complex **2** is shown in Fig. 2, with selective atom labelling Scheme. The crystal structure of complex **2** is isostructural to the complexes with general formula [CuX(PCy_3)$_2$] (X = Cl, Br, I) [1]. The geometry around the copper(I) centre is trigonal planar. The average Cu–P distance is 2.2395(8) Å, this is shorter than that found in other Cu^I complexes [1]. Whereas, the Cu–I distance 2.536(4) Å is also shorter than that found in complex [CuI(PCy_3)$_2$] [1]. The bond angles around the copper(I) centre are 133.04(3)° for P–Cu–P and 111.55(3)° and 115.37(2)° for I–Cu–P. These bond angles values show considerable deviation from the ideal trigonal planar angle of 120°.

3.1.3. *[CuCl($PPhCy_2$)$_2$] (**3**)*

The molecular structure of complex **3** is isostructural and isomorphous to complex **2**. A perspective view of the molecular structure of complex **3** is shown in Fig. 3, with selective atom labelling Scheme. The geometrical environment around the copper(I) centre is distorted trigonal planar. The Cu–Cl bond distance 2.241(2) Å is shorter than Cu–I bond distance found in complex **2** and this difference is attributed to the different atomic sizes of chlorine and iodine atoms coordinated with same type of metal centre. The Cu–P bond distances 2.250(2) and 2.257(2) Å; are longer than in complex **2**. The P–Cu–Cl bond angles are 113.33(9)° and 116.51(8)°, whereas the P–Cu–P bond angle is 130.10(9)°. Again these bond angles values show considerable deviation from the ideal trigonal planar angle of 120°.

3.1.4. *[CuBr(PPh_3)$_3$]·CH_3CN (**4**)*

A view of molecular structure of complex **4** is shown in Fig. 4, with selected atom labelling Scheme. The molecular structure of the complex is a pseudo polymorph of the complexes [CuBr(PPh_3)$_3$], [CuBr(PPh_3)$_3$]·THF, and [CuBr(PPh_3)$_3$]·$(CH_3)_2CO$ [22,62], which were all measured at room temperature. The crystallographic environment around the copper(I) atom is distorted tetrahedral, as found in the other polymorphic forms. The asymmetric unit contains one acetonitrile molecule of crystallization. The solvent molecule does not show any coordination with the metal centre and is well separated. This observation is similar to that in the other pseudo-polymorphic forms of the complex. The copper(I) centre is coordinated with three monodentate triphenyl phosphine ligand molecules and one bromine atom. The Cu–P bond distances range from 2.305(1) to 2.314(1) Å, and the Cu–Br bond distance is 2.483(1) Å. The Cu–P bond distances are slightly shorter than those found in the polymorphic forms, where these distances vary from 2.329 to 2.369 Å. The Cu–Br bond distance is longer than that found in [CuBr(PPh_3)$_3$]·THF [62], that is 2.439 Å, but shorter than that found in [CuBr(PPh_3)$_3$] and [CuBr(PPh_3)$_3$]·$(CH_3)_2CO$ [22], that is, 2.503 and 2.506 Å, respectively. These differences may in part be due to the fact that the X-ray diffraction data for complex **4** were measured at 173 K, while for the pseudo polymorphs the data were in general measured at 293 K. The bond angles values around the copper(I) atom vary from 99.05(3)° to 120.08(3)°, which indicates a distorted tetrahedral geometry around the copper(I) atom. The deviation from ideal tetrahedral geometry around the central metal atom is similar to that found in its polymorphic forms.

3.1.5. *[Ag($PPhCy_2$)$_2$(NO_3)] (**5**)*

Complex **5** crystallized in the chiral monoclinic space group $P2_1$. The geometrical environment around the silver(I) atom can be considered to be pseudo trigonal planar, with the silver(I) atom coordinated with two phosphorous atoms of the monodentate tertiary phosphine and one oxygen atom of the nitrate counter ion (Fig. 5). The Ag–P1 and Ag–P2 bond distances are 2.4043(8) and 2.4260(8) Å, respectively, and the Ag–O1 and Ag–O3 bond distances are 2.606(4) and 2.687(3) Å, respectively. The rather long Ag–O3 bond distance indicates the presence of a weak Ag–O coordination bond, hence the metal centre in this neutral complex can be considered to be four coordinate, with the anion acting as a bidentate chelating ligand. The two phosphine ligands are present in a partially eclipsed conformation with O–Ag–P bond angles of 89.74(9)° and 115.46(9)°, and a P1–Ag1–P2 bond angle of 154.25(3)°. These bond angles around the silver(I) atom show considerable deviation from the ideal trigonal planar angle of 120°.

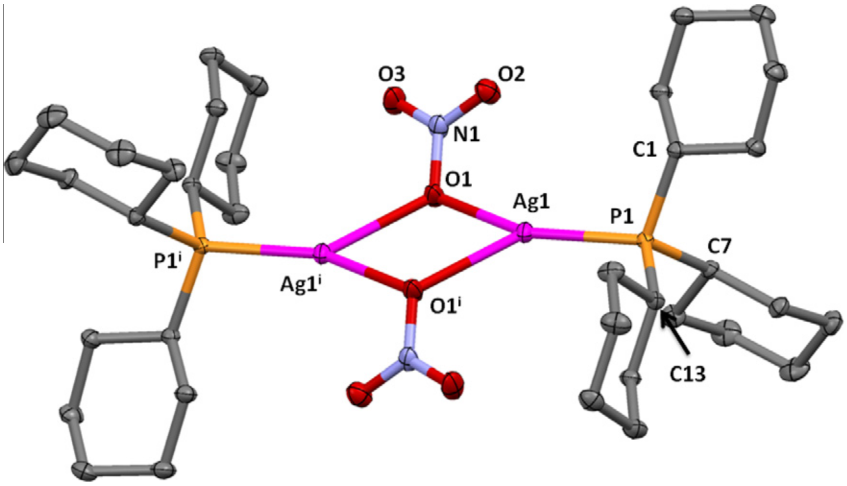

Fig. 6. A view of the molecular structure of complex with displacement ellipsoids drawn at the 30% probability level [H-atoms have been omitted for clarity].

Table 1
Summary of crystal data and structure refinement details for compounds **1–6**.

	1.2H$_2$O	**2**	**3**	**4·CH$_3$CN**	**5**	**6**
Empirical formula	$C_{72}H_{84}Cu_4I_4P_4$	$C_{36}H_{54}CuIP_2$	$C_{36}H_{54}ClCuP_2$	$C_{54}H_{45}BrCuP_3$	$C_{36}H_{54}AgNO_3P_2$	$C_{36}H_{66}Ag_2N_2O_6P_2$
Formula weight	1871.06	739.17	647.72	971.31	718.61	900.59
Crystal size (mm)	0.38 × 0.34 × 0.30	0.45 × 0.45 × 0.40	0.30 × 0.19 × 0.08	0.30 × 0.19 × 0.11	0.37 × 0.37 × 0.16	0.50 × 0.50 × 0.29
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature (K)	173	173	173	173	173	173
Crystal symmetry	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1$	$P\bar{1}$
a (Å)	13.6424(13)	10.4500(3)	10.2513(9)	11.5329(10)	10.9551(7)	9.1676(7)
b (Å)	14.1754(14)	23.4853(10)	24.433(2)	13.0973(11)	13.7042(6)	9.1338(7)
c (Å)	21.583(2)	14.6356(5)	13.9602(12)	15.7012(14)	12.2536(8)	13.3139(10)
α (°)	101.305(12)	90	90	88.859(10)	90	91.077(6)
β (°)	96.666(12)	9.586(3)	99.929(10)	83.677(10)	107.158(5)	97.359(6)
γ (°)	111.047(11)	90	90	84.956(10)	90	116.098(6)
V (Å^3)	3739.7(6)	3541.7(2)	3444.2(5)	2348.0(4)	1757.77(18)	989.39(13)
Z	2	4	4	2	2	1
D_c (Mg m^{-3})	1.662	1.386	1.249	1.374	1.358	1.512
μ(Mo Kα) (mm^{-1})	2.9	1.601	0.828	1.457	0.699	1.115
F(0 0 0)	1848	1528	1384	1000	756	468
θ Limits (°)	2.07–26.04	1.65–29.55	2.1–22.80	1.90–25.90	1.73–29.43	1.55–29.72
Measured reflections	29 409	68 504	25 811	18 563	27 426	14 354
Unique reflections (R_{int})	13 628(0.0459)	9593(0.0734)	6761(0.2323)	8580(0.0606)	9005(0.0669)	5332(0.0229)
Observed reflections	8896	8361	1925	4743	7682	5057
Goodness-of-fit (GOF) on F^2	0.824	1.186	0.71	0.76	1.022	1.084
$R_1(F)$,[a] $[I > 2\sigma(I)]$	0.0327	0.0438	0.0661	0.0319	0.0374	0.0234
wR_2 (F^2),[b] $[I > 2\sigma(I)]$	0.0684	0.099	0.1506	0.0516	0.0844	0.0593
Largest differences in peak and hole (e Å^{-3})	0.956, −0.922	0.813, −0.749	0.585, −1.108	0.466, −0.521	0.513, −0.975	0.409, −0.860

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

3.1.6. *[Ag(PCy$_3$)$_2$(NO$_3$)]$_2$ (**6**)*

Compound **6** is a centrosymmetric binuclear complex and its molecular structure is illustrated in Fig. 6. The metal centres are three coordinate with distorted trigonal planar geometry, and with the NO_3^- anion acting as an asymmetric monodentate bridging ligand. The [PAg(O)$_2$AgP] unit is planar within experimental error; the oxygen atoms bonded to the silver atoms are in-plane, while atoms N1/O2/O3 are out-of-plane. The two phosphine ligand molecules coordinated to the silver(I) atom are staggered and adopt a disposition of opposite chirality. The P–C7 bond rotates out of the [PAg(O)$_2$AgP] plane and this rotation results in an unsymmetrical interaction between the oxygen atom of the nitrate anion and the neighbouring cyclohexyl group hydrogen atoms, such that bond Ag–O1 is shorter than bond Ag–O1^i, and bond angle P–Ag–O1 is larger than angle P–Ag–O1^i (Table 2). This distortion is accommodated by dislocation of the two Cy$_3$PAgO fragments within the [PAg(O)$_2$AgP] plane.

In compound **7** the Ag–P bond length is 2.3374(4) Å and the Ag–O bond distances are 2.2475(13) and 2.4210(15) Å. The O1–Ag1–P1 and O1^i–Ag1–P1 bond angles are 155.78(4)° and 133.59(3)°, respectively. The O1–Ag–O1^i bond angle is 70.55(5)° and the bridging Ag1–O1–Ag1^i angle is 109.45(6)°, with a Ag···Ag distance of 3.8126(3) Å; shows no metal–metal interaction.

In the crystal structures of the copper(I) complexes, **1–4**, there are no classical hydrogen bonding interactions. Only in complexes **2**, **3** and **4** are there C–H···halogen interactions. In complex **1** the halogens are embedded in a cavity surrounded by the phosphine substituents. In complexes **2** and **4** two-dimensional sheet-like networks are formed, while in complex **3** a one-dimensional chain is formed. In the silver(I) complexes, **5** and **6,** there are a number of

Table 2
Selected bond distances (Å) and bond angles (°) for complex **1–6**.

Bond lengths (Å)		Bond angles (°)	
1			
I1–Cu2	2.6750(8)	Cu1–I1–Cu2	67.19(3)
I1–Cu3	2.7135(7)	Cu1–I1–Cu3	71.63(2)
I2–Cu1	2.6631(8)	Cu2–I1–Cu3	73.73(2)
I2–Cu2	2.6646(8)	Cu1–I2–Cu2	67.67(3)
I2–Cu4	2.7251(7)	Cu1–I2–Cu4	73.41(2)
I3–Cu2	2.7006(7)	Cu2–I2–Cu4	71.64(2)
I3–Cu3	2.7125(8)	Cu2–I3–Cu3	73.35(2)
I3–Cu4	2.7064(8)	Cu2–I3–Cu4	71.38(2)
I4–Cu1	2.7182(7)	Cu3–I3–Cu4	70.36(3)
I4–Cu3	2.6399(8)	Cu1–I4–Cu3	72.25(2)
I4–Cu4	2.6977(8)	Cu1–I4–Cu4	72.98(2)
Cu1–P1	2.2413(15)	Cu3–I4–Cu4	71.58(3)
Cu2–P2	2.2439(14)	I1–Cu1–I2	111.04(3)
Cu3–P3	2.2416(15)	I1–Cu1–I4	104.49(3)
Cu4–P4	2.2510(16)	I1–Cu1–P1	113.35(5)
		I2–Cu1–I4	103.21(3)
		I2–Cu1–P1	115.60(5)
		I4–Cu1–P1	107.96(4)
		I1–Cu2–I2	111.32(3)
		I1–Cu2–I3	102.20(3)
		I1–Cu2–P2	117.53(5)
		I2–Cu2–I3	106.57(3)
		I2–Cu2–P2	108.86(4)
		I3–Cu2–P2	109.68(4)
		I1–Cu3–I3	100.90(3)
		I1–Cu3–I4	105.89(3)
		I1–Cu3–P3	114.37(5)
		I3–Cu3–I4	108.63(3)
		I3–Cu3–P3	112.07(5)
		I4–Cu3–P3	113.98(4)
		I2–Cu4–I3	104.72(3)
		I2–Cu4–I4	102.11(3)
		I2–Cu4–P4	114.21(4)
		I3–Cu4–I4	107.13(3)
		I3–Cu4–P4	112.27(5)
		I4–Cu4–P4	115.35(4)
2			
I1–Cu1	2.5360(5)	I1–Cu1–P1	115.37(2)
Cu1–P1	2.2392(9)	I1–Cu1–P2	111.55(3)
Cu1–P2	2.2399(8)	P1–Cu1–P2	133.04(3)
3			
Cu1–Cl1	2.241(2)	Cl1–Cu1–P1	113.33(9)
Cu1–P1	2.250(2)	Cl1–Cu1–P2	116.51(8)
Cu1–P2	2.257(2)	P1–Cu1–P2	130.10(9)
4			
Br1–Cu1	2.4826(5)	Br1–Cu1–P1	105.53(3)
Cu1–P1	2.3112(9)	Br1–Cu1–P2	99.05(3)
Cu1–P2	2.3045(9)	Br1–Cu1–P3	101.63(3)
Cu1–P3	2.3138(10)	P1–Cu1–P2	112.70(4)
		P1–Cu1–P3	114.56(4)
		P2–Cu1–P3	120.08(3)
5			
Ag1–P1	2.4043(8)	P1–Ag1–P2	154.25(3)
Ag1–P2	2.4261(9)	P1–Ag1–O1	115.47(9)
Ag1–O1	2.606(4)	P2–Ag1–O1	89.74(9)
Ag1–O3	2.687(3)		
6			
Ag1···Ag1^{i}	3.8126(3)	Ag1–O1–Ag1^{i}	109.45(6)
Ag1–P1	2.3374(4)	P1–Ag1–O1	155.78(4)
Ag1–O1	2.2475(13)	P1–Ag1–O1^{i}	133.60(3)
Ag1–O1^{i}	2.4210(15)	O1–Ag1–O1^{i}	70.55(5)

Symmetry codes: (i) 2 − *x*, 1 − *y*, 1 − *z*.

C–H···O interactions involving the nitrate O-atoms, which lead to the formation of one-dimensional chains.

3.2. ^{1}H, ^{13}C and ^{31}P NMR Spectroscopic studies

The IR spectra of compounds **1–6** have been recorded in the range of 4000–450 cm^{-1} and are characterized by many absorption bands of the coordinated tertiary phosphine ligands, apart from the characteristic bands for aromatic and non-aromatic hydrogen 2900–3100 cm^{-1} for all complexes. For complexes **1** and **4**, several stretching bands are also observed in the spectra.

In the ^{1}H and ^{13}C NMR spectra of complexes **1–3** no classical variation has been observed. The pattern of cyclohexyl and phenyl resonances is similar to those reported for a silver(1) and gold(I) complex [63,64,39].

In ^{31}P NMR of compound **1,** a sharp singlet was observed for diphenylcyclohexyl phosphine at −9.3 ppm, which is 3 ppm down field compared to the free phosphine (∼−6.12 ppm). In ^{31}P NMR of compound **2** and **3**, sharp single peaks were observed at 6.3 ppm for dicyclohexylphenyl phosphine, those are about ∼37 ppm downfield compared to free phosphine (∼43.1 ppm). This type of behaviour of ^{31}P NMR is well documented [39]. The ^{31}P NMR spectra of complexes of silver(I) with phosphorous-donor ligands may show splitting due to ^{1}J(P–Ag) coupling. In the ^{31}P NMR spectra of complex **5** two well defined doublet peaks were observed at 24.1 and 27.1 ppm, about 23, and 26 ppm, respectively, downfield compared to the uncomplexed dicyclohexylphenyl phosphine (∼1 ppm). In the ^{31}P NMR of compound **6**, the resonance for the coordinated tricyclohexyl phosphine appear as an intense doublet peak at 42.3 ppm, about 34 ppm, downfield compared to the uncomplexed tricyclohexyl phosphine (∼8 ppm). Silver(I) complexes with (1:2, and 1:1 stoichiometric ratio) show well resolved pairs of doublets, the resolution of signals for 1:2 and 1:1 species is due to ^{1}J(P–Ag) coupling (^{1}J(P–Ag) = 1200 and ^{1}J(P–Ag) = 1040 MHz respectively for compounds **5** and **6**). The ^{31}P NMR spectral results are in agreement with the previously reported silver(I) phosphine complexes [22,30–54,63,65].

4. Conclusions

X-ay diffraction studies of complexes **1–6** suggest that the geometrical environment around the Cu^{I} and Ag^{I} centres is highly dependent on the stoichiometric ratio of the reactants, the type of phosphines used (cyclohexyl or phenyl groups), the counter ions, and the solvent of crystallization. The use of cyclohexyl type phosphines resulted in trigonal planar geometry around the metal centre in compounds **2**, **3**, **5**, and **6**. For compounds **2** and **3** the sum of the halide–Cu–P angles, while deviating from the standard angle of 120°, add up to ca. 360°. In compound **5** the P–Ag–O and O–Ag–P angles also add up to ca. 360° and in compound **6** the P–Ag–O and O–Ag–O angles also add up to ca. 360°.

The use of phenyl type phosphines resulted in distorted tetrahedral geometry in compounds **1** and **4**. Here the sum of the halide–Cu–P angles varies from ca. 336.0–341.8° in compound **1**, while in compound **4** this sum is only ca. 296.2°, indicating considerable deformation of the copper(I) coordination sphere in both compounds. In the ^{31}P NMR spectra of compounds **1–3, 5–6**, a down field shift was observed. In the ^{31}P NMR spectra of the silver(I) complexes, **5** and **6**, doublet peaks were observed due to ^{1}J(P–Ag) coupling, while for the copper(I) complexes only sharp singlet peaks were present. The silver(I) and copper(I) complexes, **1–6**, were synthesized as precursors to explore the mixed ligand chemistry of coin metal(I) coordination compounds [66].

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Appendix A. Supplementary material

Supplementary crystallographic data of compounds **1–6** (CCDC No. 739417–739419, 739421, 751728–751729) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.04.031.

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