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# Copper(I) halide complexes from *cis*-1,2-bis(diphenylphosphino) ethylene and some heterocyclic thiones

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## Abstract

Reaction of copper(I) chloride or bromide with equimolar amounts of the diphos ligand *cis*-1,2-bis(diphenylphosphino)ethylene (dppet) and a heterocyclic thione (L) in acetonitrile/methanol solvent afforded mononuclear complexes of the type [CuX(dppet)(L)] with the diphosphine ligand acting as a chelating ligand. However, the same reaction carried out at higher temperatures proceeds, in some cases, with exclusion of the phosphine ligand from the coordination sphere leading to double-S-bridged dimers. In contrast, copper(I) iodide under the same conditions gave the thione-free dimeric compound $[CuI(dppet)]_2$ which contains double-bridging iodine atoms. A notable exception was for the reaction with 5-methyl-1,3,4-thiadiazole-2-thione (mtdztH) which, under the same conditions, gave rise to the unexpected, simultaneous formation of the monomer $[CuI(dppet)(CH_3CN)]$ as well as the above mentioned dimeric $[CuI(dppet)]_2$. Furthermore treatment [CuX(dppet)(L)] with two equivalents of triphenylphosphine was found to cause replacement of the diphos ligand, while substitution of the chlorine atom under HCl elimination and formation of $[Cu(dppet)(mftztH)_2]$ occured in the unique case of treating [CuCl(dppet)(mftztH)] with one additional equivalent of the same thione ligand. The structures of one representative for each of the above mentioned types of complexes, namely [CuBr(dppet)(mftztH)], $[Cu(dppet)(mftztH)_2]$, $[Cu(\mu\text{-}I)(dppet)]_2 \cdot [CuI(dppet)(CH_3CN)]$ and $[CuBr\{\mu\text{-}S(pymtH)\}(pymtH)]_2$ have been established by single-crystal X-ray diffraction.

*Keywords:* Copper(I) complexes; *cis*-1,2-Bis(diphenylphosphino)ethylene complexes; Heterocyclic thione complexes; Crystal structures

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## 1. Introduction

The interaction of the low valent coinage metals with both tertiary arylphosphines and heterocyclic thiones have been the focus of a considerable amount of work for some time. Owing to their application in catalytic functions [1–3] phosphine containing transition metal complexes have received widespread attention, whereas the significance of heterocyclic thiones, as ligands in metal complexes, stems from their relevance in biological systems [4]. As a contribution to this field of research we have been engaged in the study of the mixed ligand copper(I) halide complexes blending both heterocyclic thione and tertiary arylphosphine ligands [5–11]. Considering that neutral thione molecules with both nitrogen and sulfur as potential donating atoms can be coordinated to a metal in a rich variety of ways, it is noteworthy that in the complexes structurally characterized by us, the copper(I) centre is bound exclusively through the exocyclic sulfur atom either in a terminal or bridging mode. Nonetheless, an outstanding variety of structures ranging from mononuclear three- or four-coordinate species with trigonal planar and tetrahedral Cu(I), respectively, to double bridged dimers in which the two copper centers are linked either by a double halide or by a double thione-sulfur bridge were obtained even within a closely related series of thione ligands. In the course of our investigations, much effort has been devoted to understanding the factors which affect the stoichiometric and structural preferences of these complexes. In the case of dimeric species of general formula

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$[CuX(PR_3)(thione)]_2$, for example, the coordination behaviour (terminal or bridging mode) of each ligand should depend on the nature of the halogen present. Thus, formation of halogen-bridges has been found to be prefered rather for the "soft" iodine than for the "harder" chlorine base [7,8].

Recently we started a comparative study into the substitution of unidentate triarylphosphines with flexible oligomethylene-backboned diphosphines with a view to forming chelated products. Using 1,3-bis(diphenylphosphino)propane, two different types of compounds have been observed: monomeric with tetrahedrally coordinated Cu(I) for $X = Cl$ and Br but dimeric with double bridging iodine atoms for $X = I$. These form even under the same preparative conditions, confirming once more the strong tendency of copper(I) to bind the "soft" iodine [12]. Note that this tendency in the above mentioned case is strong enough to cause the exclusion of the thione ligand from the coordination sphere. In order to obtain further information on this very interesting aspect we have now investigated the behaviour of rigid diphosphine *cis*-1,2-bis(diphenylphosphino)ethylene (dppet) towards coordination of Cu(I) halides in the presence of several heterocyclic thione ligands.

## 2. Experimental

### 2.1. Materials and instruments

Commercially available copper(I) chloride, copper(I) bromide, copper(I) iodide and *cis*-1,3-bis(diphenylphosphino)ethylene were used as received, while the thiones (Merck or Aldrich) were recrystallized from hot ethanol prior to their use. All the solvents were purified by respective suitable methods and allowed to stand over molecular sieves. Infra-red spectra in the region of 4000–250 $cm^{-1}$ were obtained in KBr discs with a Perkin–Elmer 1430 spectrophotometer, while a Perkin–Elmer-Hitachi 200 spectrophotometer was used to obtain the electronic absorption spectra. $^1H$ NMR spectra were recorded on a Brucker AM 300 spectrometer at 25 °C with positive chemical shifts given downfield from TMS. Melting points were measured in open tubes with a STUART scientific instrument and are uncorrected. Molar conductivities, magnetic susceptibility measurements and elemental analyses for carbon, nitrogen and hydrogen were performed as described previously [4].

### 2.2. X-ray crystallographic study

Single crystals suitable for crystal structure analysis were obtained by slow evaporation of acentonitrile/methanol solutions of the complexes at room temperature. X-ray diffraction data were collected on an Enraf–Nonius Kappa CCD area-detector diffractometer. The programs DENZO [13] and COLLECT [14] were used in data collection and cell refinement. Details of crystal and structure refinement are shown in Table 1. The structures were solved using program SIR97 [15] and refined with program SHELX-97 [16]. Molecular plots were obtained with program ORTEP-3 [17].

### 2.3. Computational

Extended Hückel calculations were performed using the CACAO program [18]. The calculations were carried out using crystallographic data of the studied molecules. The EHT parameters for Cu were those established in the literature.

### 2.4. Synthesis of complexes **1–13**

The complexes were prepared according to the following general procedure. A suspension of copper(I) halide (0.5 mmol) and *cis*-1,2-bis(diphenylphosphino)ethylene (198.2 mg, 0.5 mmol) in 20 $cm^3$ acetonitrile was stirred until a white precipitation was formed. A solution of the appropriate thione (0.5 mmol) in methanol was then added and the new suspension was stirred to clearness. The resulting solution was filtered off and the clear solution was kept at room temperature. Slow evaporation of the solvent at room temperature gave the microcrystalline solid, which was filtered off and dried in vacuo.

### 2.5. Synthesis of $[Cu(dppet)(mftztH)_2]$ (**14**)

An acetonitrile/methanol solution of [CuCl(dppet)(mftztH)] (**4**) (133 mg, 0.2 mmol) was treated with equimolar amount of mftzH (34 mg, 0.2 mmol) and refluxed for 30 min. The resulting clear solution was filtered off and kept at room temperature. Slow evaporation of the solvent at room temperature gave the crystalline solid, which was filtered off and dried in vacuo.

### 2.6. Synthesis of complexes **15–16**

The two phosphane-free compounds were prepared by refluxing equimolar quantities of copper(I) chloride or bromide, *cis*-1,2-bis (diphenylphosphino)ethylene and pyrimidine-2-thione in dry acetonitrile or acetone (30 ml) for 2 h and subsequent slow evaporation of the resulting clear solution at room temperature. Alternatively, refluxing of compound **2** or **8** in dry acetonitrile for 4 h gave a clear yellow solution. Slow evaporation of the solvent at room temperature gave the crystalline solid, which was filtered off and dried in vacuo.

Table 1
Crystal data and structure refinements for [CuBr(dppet)(mftztH)] (**9**), [Cu(dppet)(mftztH) (mftzt)] (**14**), [Cu(μ-I)(dppet)]$_2$ [CuI(dppet)(CH$_3$CN)] (**13**) and [CuBr{μ-S(pymtH}(pymtH)]$_2$ (**16**)

| | **9** | **14** | **13** | **16** |
|---|---|---|---|---|
| Chemical formula | $C_{30}H_{26}BrCuF_3N_3P_2S$ | $C_{34}H_{29}CuF_6N_6P_2S_2$ | $C_{52}H_{44}Cu_2I_2P_4 \cdot C_{28}H_{25}$-$CuINP_2 \cdot C_2H_3N$ | $C_{16}H_{16}Br_2Cu_2N_8S_4$ |
| Formula weight | 722.99 | 825.23 | 1842.56 | 735.51 |
| Temperature (K) | 120(2) | 120(2) | 120(2) | 120(2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | triclinic | monoclinic | monoclinic | triclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ | $P2_1/c$ | $P\bar{1}$ |
| *a* (Å) | 9.8429(2) | 11.384(5) | 18.1463(2) | 8.1729(2) |
| *b* (Å) | 11.3450(4) | 18.927(5) | 12.04760(10) | 8.9811(3) |
| *c* (Å) | 14.6006(5) | 17.303(5) | 35.9323(4) | 9.2616(3) |
| α (°) | 100.6860(10) | 90 | 90 | 82.2910(10) |
| β (°) | 106.870(2) | 104.6900(11) | 98.9870(10) | 70.5960(10) |
| γ (°) | 98.312(2) | 90 | 90 | 68.866(2) |
| Volume (Å$^3$) | 1498.69 (8) | 3606(2) | 7759.06(14) | 598.00(3) |
| *Z* | 2 | 4 | 4 | 1 |
| Density (calculated) (mg/m$^3$ Å) | 1.602 | 1.520 | 1.577 | 2.042 |
| Absorption coefficient (mm$^{-1}$) | 2.283 | 0.876 | 2.176 | 5.491 |
| *F*(0 0 0) | 728 | 1680 | 3656 | 360 |
| Crystal size (mm) | 0.22 × 0.14 × 0.06 | 0.15 × 0.10 × 0.10 | 0.30 × 0.18 × 0.08 | 0.16 × 0.16 × 0.10 |
| θ range for data collection (°C) | 2.98–27.54 | 3.25–27.48 | 2.92–27.52 | 3.03–27.51 |
| Index ranges | $-12 \leqslant h \leqslant 12$<br>$-14 \leqslant k \leqslant 14$<br>$-18 \leqslant l \leqslant 18$ | $-14 \leqslant h \leqslant 9$<br>$-24 \leqslant k \leqslant 23$<br>$-22 \leqslant l \leqslant 22$ | $-23 \leqslant h \leqslant 19$<br>$-15 \leqslant k \leqslant 13$<br>$-46 \leqslant l \leqslant 44$ | $-10 \leqslant h \leqslant 10$<br>$-11 \leqslant k \leqslant 11$<br>$-11 \leqslant l \leqslant 11$ |
| Reflections collected | 20 847 | 28 993 | 54 016 | 5066 |
| Independent reflections | 6822 ($R_{int} = 0.0810$) | 8253 ($R_{int} = 0.1494$) | 17665 ($R_{int} = 0.0828$) | 2715 ($R_{int} = 0.0310$) |
| Completeness | 98.7% ($\theta = 27.54°$) | 99.7% ($\theta = 27.48°$) | 98.8% ($\theta = 27.48°$) | 98.6% ($\theta = 27.51°$) |
| Data [$(I > 2\sigma(I))$]/ restrains/parameters | 6822/0/371 | 8253 /0/462 | 17665/0/867 | 2715/0/145 |
| Maximum and minimum transmission | 0.8752 and 0.6336 | 0.9175 and 0.8798 | 0.8451 and 0.5613 | 0.6097 and 0.4736 |
| Refinement method | full-matrix l.s. on $F^2$ | full-matrix l.s. on $F^2$ | full-matrix l.s. on $F^2$ | full-matrix l.s. on $F^2$ |
| Goodness-of-fit on $F^2$ | 1.026 | 1.020 | 0.990 | 1.024 |
| Final *R* indices [$(I > 2\sigma(I)$] | $R_1 = 0.0373$,<br>$wR_2 = 0.0811$ | $R_1 = 0.0697$,<br>$wR_2 = 0.1479$ | $R_1 = 0.0425$,<br>$wR_2 = 0.0938$ | $R_1 = 0.0387$<br>$wR_2 = 0.0860$ |
| *R* indices (all data) | $R_1 = 0.0589$,<br>$wR_2 = 0.0878$ | $R_1 = 0.1326$,<br>$wR_2 = 0.1771$ | $R_1 = 0.0704$,<br>$wR_2 = 0.1043$ | $R_1 = 0.0549$,<br>$wR_2 = 0.0921$ |
| Final weighting scheme[a] | $a = 0.0473$, $b = 0.0407$ | $a = 0.0604$, $b = 0.0245$, | $a = 0.0473$, $b = 0.0000$, | $a = 0.0476$, $b = 0.0000$ |
| Largest difference peak and hole (e Å$^3$) | 0.457 and −0.764 | 0.680 and −1.090 | 1.122 and −1.352 | 0.676 and −0.836 |

[a] Calc. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP)$, where $P = (F_o^2 + 2F_c^2)/3$.

### *2.6.1. [CuCl(dppet)(py2SH)] (**1**)*

Orange crystals (203 mg, 67%), m.p. 138 °C; *Anal.* Calc. for $C_{31}H_{27}ClCuNP_2S$: C, 61.38; H, 4.49; N, 2.31; Found: C, 62.16; H, 4.55; N, 2.20%; IR (cm$^{-1}$): 3032w, 1652s, 1580vs, 1481s, 1434vs, 1370s, 1185s, 1133vs, 1099s, 1025m, 992s, 743vs, 693vs, 538vs, 485s, 448s; UV–Vis ($\lambda_{max}$, $\log \varepsilon$): (CHCl$_3$): 248.5 (4.31), 295.0 (4.25), 398.5 (3.19).

### *2.6.2. [CuCl(dppet)(pymtH)] (**2**)*

Orange-red crystals (235 mg, 74%), m.p. 135 °C; *Anal.* Calc. for $C_{30}H_{26}ClCuN_2P_2S$: C, 59.31; H, 4.31; N, 4.61; Found: C, 59.67; H, 4.41; N, 4.61%; IR (cm$^{-1}$): 3043w, 1604s, 1598vs, 1480vs, 1434vs, 1327vs, 1215s, 1176vs, 1098s, 976s, 744vs, 693vs, 539vs, 481s; UV–Vis ($\lambda_{max}$, $\log \varepsilon$), (CHCl$_3$): 248.5 (4.31), 295.0 (4.25), 398.5 (3.19).

### *2.6.3. [CuCl(dppet)(mtdztH)] (**3**)*

Yellow crystals (185 mg, 59%), m.p. 153 °C; *Anal.* Calc. for $C_{29}H_{26}ClCuN_2P_2S_2$: C, 55.50; H, 4.18; N, 4.46; Found: C, 56.05; H, 4.29; N, 4.52%; IR (cm$^{-1}$): 3042w, 1636s 1465m, 1433s, 1268s, 1185s, 1097m, 1051s, 730vs, 692vs, 618m, 540vs, 484s; UV–Vis ($\lambda_{max}$, $\log \varepsilon$): (CHCl$_3$); 248.5 (4.30), 306.0 (4.31); $^1$H NMR (CDCl$_3$, δ ppm): 13.90 (br, 1H, NH$_{mtdztH}$), 7.12–7.88 (m, 22H, $C_6H_5$ + –CH=CH–), 2.45 (s, 3H, $CH_3$–C).

### *2.6.4. [CuCl(dppet)(mftztH)] (**4**)*

Yellow crystals (153 mg, 45%), m.p. 186 °C; *Anal.* Calc. for $C_{30}H_{26}ClCuF_3N_3P_2S$: C, 53.10; H, 3.86; N, 6.19; Found: C, 53.77; H, 4.22; N, 6.19%; IR ($cm^{-1}$): 3028m, 1652s, 1480vs, 1435vs, 1280vs, 1203vs, 1147vs, 1091vs, 731vs, 693vs, 579s, 541vs, 471vs; UV–Vis ($\lambda_{max}$, $\log\varepsilon$): ($CHCl_3$); 253.0 (4.36), 293.5 (4.01); $^1$H NMR ($CDCl_3$, $\delta$ ppm):14.05 (br, 1H, $NH_{mtdztH}$), 7.06–7.67 (m, 22H, $C_6H_5$ + –CH=CH–), 3.58 (s, 3H, $CH_3$–N).

### *2.6.5. [CuCl(dppet)(bzoxtH)] (**5**)*

Pale yellow crystals (187 mg, 58%), m.p. 134 °C; *Anal.* Calc. for $C_{33}H_{27}ClCuNP_2OS$: C, 61.30; H, 4.21; N, 2.17; Found: C, 61.26; H, 4.19; N, 2.26%; IR ($cm^{-1}$): 3042w, 1634s, 1511vs, 1480s, 1448vs, 1434vs, 1252s, 1191s, 1142vs, 1093s, 932s, 732vs, 695vs, 540vs, 476s, 424m; UV–Vis ($\lambda_{max}$, $\log\varepsilon$): ($CHCl_3$); 245.0 (4.11), 302.0 (4.25); $^1$H NMR ($CDCl_3$, $\delta$ ppm): 13.95 (br, 1H, $NH_{bzoxtH}$); 7.12–7.87 (m, 26H, $C_6H_5$ + –CH=CH–).

### *2.6.6. [CuCl(dppet)(mbzimtH$_2$)] (**6**)*

Yellow crystals (191 mg, 58%), m.p. 138 °C; *Anal.* Calc. for $C_{34}H_{30}ClCuN_2P_2S$: C, 61.91; H, 4.58; N, 4.25; Found: C, 62.18; H, 4.77; N, 4.48%; IR ($cm^{-1}$): 3046w, 1616s, 1514s, 1457vs,1438vs, 1374s, 1325vs, 1183vs, 1097vs, 998s, 802s, 740vs, 697vs, 630s, 542vs, 470s, 392m; UV–Vis ($\lambda_{max}$, $\log\varepsilon$): ($CHCl_3$); 251.5 (4.36), 308.5 (4.38); $^1$H NMR ($CDCl_3$, $\delta$ ppm): 10.45 (br, 2H, $NH_{mbzimtH2}$); 6.91–7.65 (m, 25H, $PC_6H_5$+ PCH = CHP, +$CH_{mbzimtH2}$), 2.28 (s, 3H, $CH_3-C_{Ph}$).

### *2.6.7. [CuBr(dppet)(py2SH)] (**7**)*

Yellow crystals (202 mg, 62%), m.p. 153 °C; *Anal.* Calc. for $C_{31}H_{27}BrCuNP_2S$: C, 57.19; H, 4.18; N, 2.15; Found: C, 57.10; H, 4.23; N, 2.08%; IR ($cm^{-1}$): 3046w, 1606s, 1574vs, 1480s, 1433vs, 1370s, 1183s, 1132vs,1098vs, 992s 743vs, 692vs, 538vs, 483s, 447s; UV–Vis ($\lambda_{max}$, $\log\varepsilon$): ($CHCl_3$): 248.0 (4.25), 296.5 (4.21), 386.5 (3.79); $^1$H NMR ($CDCl_3$, $\delta$ ppm): 14.35 (br, 1H, $NH_{py2SH}$), 7.62–7.26 (m 25H, $C_6H_5$ + –CH=CH– + $CH_{py2SH}$), 6.73 (t, 1H, $CH_{py2SH}$).

### *2.6.8. [CuBr(dppet)(mtdztH)] (**8**)*

Yellow crystals (171 mg, 51%), m.p. 141 °C; *Anal.* Calc. for $C_{29}H_{26}BrCuN_2P_2S_2$: C, 51.83; H, 3.90; N, 4.17; Found: C, 52.19; H, 4.10; N, 4.26%; IR ($cm^{-1}$): 3048w, 1636m, 1481s, 1457m, 1433vs, 1265s, 1158m, 1097s, 1054s 740vs, 692vs, 515vs, 515s, 470m; UV–Vis ($\lambda_{max}$, $\log\varepsilon$): ($CHCl_3$); 246.0 (4.14), 307.0 (4.04); $^1$H NMR ($CDCl_3$, $\delta$ ppm): 13.82 (br, 1H, $NH_{mtdztH}$), 7.60–7.06 (m, 22H, $C_6H_5$ + –CH=CH–), 2.41 (s, 3H, $CH_3$–C).

### *2.6.9. [CuBr(dppet)(mftztH)] (**9**)*

Yellow crystals (246 mg, 68%), m.p. 204 °C; *Anal.* Calc. for $C_{30}H_{26}BrCuF_3N_3P_2S$: C, 49.84; H, 3.62; N, 5.81; Found: C, 50.05; H, 3.62; N, 5.77%; IR ($cm^{-1}$): 3018w, 1618m, 1583m, 1480vs, 1436vs, 1278vs, 1206s, 1154s, 1093vs, 734vs, 696vs, 541vs, 517s, 475s, 432m; UV–Vis ($\lambda_{max}$, $\log\varepsilon$): ($CHCl_3$); 255.0 (4.39), 298.5 (4.09); $^1$H NMR ($CDCl_3$, $\delta$ ppm): 14.25 (br, 1H, $NH_{mtdztH}$), 7.07–7.69 (m, 22H, $C_6H_5$ + –CH=CH–), 3.55 (s, 3H, $CH_3$–N).

### *2.6.10. [CuBr(dppet)(bzoxtH)] (**10**)*

Brown crystals (197 mg (57%), m.p. 198 °C; *Anal.* Calc. for $C_{33}H_{27}BrCuNP_2OS$: C, 57.36; H, 3.94; N, 2.03; Found: C, 57.12; H, 3.95; N, 1.97%; IR ($cm^{-1}$): 3040w, 1616s, 1511vs, 1480vs, 1434vs, 1284s, 1252vs, 1187s, 1140vs, 1099vs, 934vs, 749vs, 732vs, 696vs, 540vs, 476s, 423s; UV–Vis ($\lambda_{max}$, $\log\varepsilon$): ($CHCl_3$); 245.0 (3.99), 306.0 (4.11); $^1$H NMR ($CDCl_3$, $\delta$ ppm): 13.65 (br, 1H, $NH_{bzoxtH}$); 7.13–7.56 (m, 26H, $C_6H_5$ + –CH=CH– + $CH_{bzoxtH}$).

### *2.6.11. [CuBr(dppet)(mbzimtH$_2$)] (**11**)*

Yellow crystals (162 mg, 46%), m.p. 140 °C; *Anal.* Calc. for $C_{34}H_{30}BrCuN_2P_2S$: C, 58.00; H, 4.29; N, 3.98; Found: C, 58.92; H, 4.26 N, 3.97%; IR ($cm^{-1}$): 3047w, 1615s, 1512s, 1481vs, 1434vs, 1374s, 1324s, 1181vs, 1098vs, 998s, 802s, 741vs, 692vs, 628s, 541vs, 514s, 391s; UV–Vis ($\lambda_{max}$, $\log\varepsilon$): ($CHCl_3$); 246.0 (4.09), 313.5 (4.13); $^1$H NMR ($CDCl_3$, $\delta$ ppm): 11.35 (br, 2H, $NH_{mbzimtH2}$); 6.86–7.52 (m, 25H, $PC_6H_5$ + PCH=CHP, +$CH_{mbzimtH2}$), 2.14 (s, 3H, $CH_3-C_{Ph}$).

### *2.6.12. [CuI(dppet)]$_2$ (**12**)*

Colourless crystals (202 mg, 69%), m.p. 241 °C; *Anal.* Calc. for $C_{52}H_{44}Cu_2I_2P_4$: C, 53.21; H, 3.78; Found: C, 53.29; H, 3.84%; IR ($cm^{-1}$): 3046w, 1606w, 1480s, 1433vs, 1370s, 1183s, 1132vs,1098vs, 992s 743vs, 692vs, 538vs, 483s, 447s; UV–Vis ($\lambda_{max}$, $\log\varepsilon$): ($CHCl_3$): 248.0 (4.25), 296.5 (4.21); $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.42–6.89 (m, $C_6H_5$ + –CH=CH–).

### *2.6.13. [CuI(dppet)(CH$_3$CN)] · [CuI(dppet)]$_2$ CH$_3$ CN (**13**)*

Yellow crystals (120 mg, 39%), m.p 240 °C, *Anal.* Calc. for $C_{82}H_{72}Cu_3I_3N_2P_6$: C, 53.11; H, 3.94; N, 1.52; Found: C, 53.11; H, 3.73; N, 1.46%; IR ($cm^{-1}$): 3031w, 1606s, 1558s, 1474s, 1426s, 1331s, 1191s, 984s, 722m, 732vs, 691vs, 541vs, 511s, 469s; UV–Vis ($\lambda_{max}$, $\log\varepsilon$): ($CHCl_3$); 248.0 (4.17), 306.0 (4.40); $^1$H NMR ($CDCl_3$, $\delta$ ppm): 7.13–7.67 (mm 66H, $C_6H_5$), 2.00 (s, 3H, $H_3C$–CN).

### *2.6.14. [Cu(dppet)(mftztH)(mftzt)] (**14**)*

Yellow crystals (67 mg, 42%), m.p. 232.5 °C; *Anal.* Calc. for $C_{34}H_{29}CuF_6N_6P_2S_2$: C, 49.49; H, 3.54; N, 10.18; Found: C, 49.46; H, 3.64; N, 10.15%; IR ($cm^{-1}$): 3054w, 1585m, 1526vs, 1482vs, 1435vs, 1258vs, 1202vs, 1144vs, 1090vs, 758s, 735vs, 695vs, 532vs, 519s, 468s, 349m; UV–Vis ($\lambda_{max}$, $\log\varepsilon$): ($CHCl_3$); 256.5 (4.12), 289.0

(3.89); $^1$H NMR (CDCl$_3$, $\delta$ ppm): 10.94 (br, 1H, NH$_{mtdztH}$), 7.71–7.69 (m, 22H, $C_6H_5$ + –CH=CH–), 2.32 (s, 3H, $CH_3$–C).

### 2.6.15. *[CuCl{μ-S(pymtH)}(pymtH)]$_2$ (**15**)*

Violet crystals (103 mg 32%), m.p. 242 °C; *Anal.* Calc. for $C_{16}H_{16}Cl_2Cu_2N_8S_4$: C, 29.72; H, 2.49; N, 17.33; Found: C, 29.10; H, 2.28; N, 17.12%; IR (cm$^{-1}$): 3059w, 1583s, 1493vs, 1419vs, 1316s, 1171s, 998vs, 789vs, 740vs, 464s, 406s; UV–Vis ($\lambda_{max}$, log $\varepsilon$): (CHCl$_3$); 248.5 (4.31), 313.0, (4.14), 429.5 (3.20).

### 2.6.16. *[CuBr{μ-S(pymtH)}(pymtH)]$_2$ (**16**)*

Violet crystals (103 mg, 28%), m.p. 223.5 °C; *Anal.* Calc. for $C_{16}H_{16}Br_2Cu_2N_8S_4$: C, 26.13; H, 2.19; N, 15.23; Found: C, 26.25; H, 2.21; N, 15.20%; IR (cm$^{-1}$): 3046m, 1598vs, 1564vs, 1481vs, 1420vs, 1322vs, 1218s, 1179vs, 1097s, 980s, 784s, 770vs, 742vs, 636m, 470s, 459s, 385s; UV–Vis ($\lambda_{max}$, log $\varepsilon$): (CHCl$_3$); 243.5 (2.86), 293,0 (2.86), 410.5 (2.79).

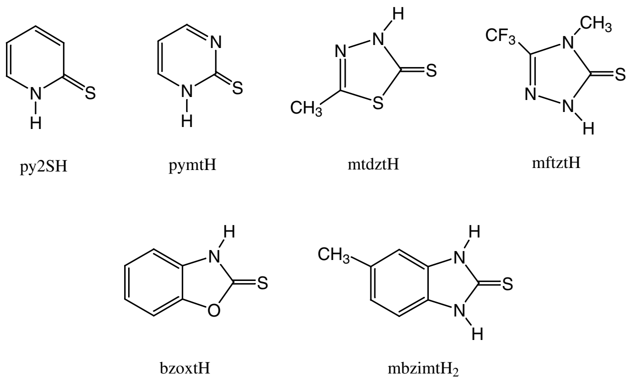
## 3. Results and discussion

### 3.1. General considerations

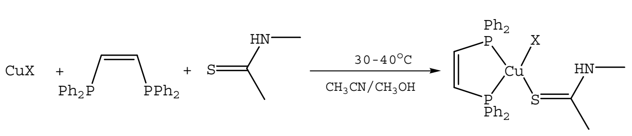
Diphosphines are generally good candidates for bridging or chelation of low oxidation state transition metal centers. Among the acyclic diphosphines of the type $Ph_2P(CH_2)_nPPh_2$, 1,2-bis(diphenylphosphino)ethane (dppe) was used for our first attempt to chelate copper(I), but it was an inappropriate choice, since dppe appears to act as a bridging, rather than as a chelating, ligand [19]. However, using the larger 1,3-bis(diphenylphosphino)propane (dppp) we recently succeeded in chelating Cu(I) [12], and we now focus once more on five-membered chelate rings including *cis*-1,2-bis(diphenylphosphino)ethylene (dppet) in our investigations.

The reaction of equimolar quantities of copper(I) chloride or bromide and *cis*-1,2-bis(diphenylphosphino)-ethylene (dppet) followed by the addition of one equivalent of the apropriate thione (L) [L = pyridine-2-thione (py2SH), pyrimidine-2-thione (pymtH), 5-methyl-1,3, 4-thiadiazole-2-thione (mtdztH), 4-methyl-5-trifluoromethyl-4H-1,2,4-triazoline-3(2H)-thione (mftztH), benz-1,3-oxazoline-2-thione (bzoxtH) and 5-methyl-benz-1, 3-imidazole-2-thione (mbzimtH$_2$) (Scheme 1) in dry acetonitrile/methanol solution at 30 °C afforded monomeric mixed ligand complexes of the type [CuX(dppet)L] (compounds **1**–**11**, Scheme 2).

During the preparation stage we noticed that the formation of the above mixed-ligand complex was related to the reaction temperature, such that the desired product was only obtained when the temperature was kept below 40 °C. Hence, a major objective of the present work was to explore the reaction course in somewhat more detail. Moreover, efforts were made to obtain crystal structures not only for key complexes but also for related products obtained during this exploration.



Scheme 1. The heterocyclic thione ligands used with their abbreviations.

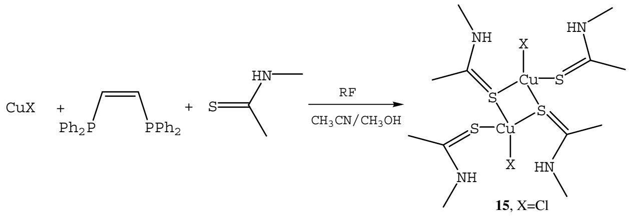


**1-11**, X=Cl, Br

Scheme 2.

Initially we investigated the influence of temperature. A mixture of CuCl or CuBr with one equivalent of both dppet and the appropriate thione was refluxed for two hours in a 1:1 acetonitrile/methanol mixture. The identity of the amorphous solid that occurred during the subsequent evaporation at ambient temperature of the resulting clear solution could, however, not be confirmed by elemental analysis or spectroscopy. The composition depended on the state of the evaporation, indicating the presence of a mixture of two or more products. Only in the case of L = pymtH were dark violet crystals of the pure phosphane-free dimers [CuX{μ-S(pymtH)}(pymtH)]$_2$ (compounds **15** and **16**) isolated during the initial stages of the evaporation (Scheme 3).

In addition, examining the influence of the rations of the thione applied, solutions of the monomeric copper(I)



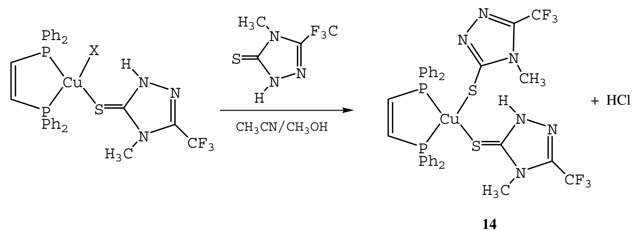
**15**, X=Cl
**16**, X=Br

Scheme 3.

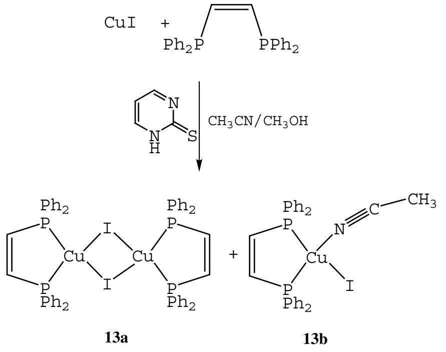
chloride complexes were treated with a two- or threefold excess of the apropriate thione ligand, with no effect such as phosphine substitution, even at higher temperatures. In one unique case, however, treatment of a $CH_3CN$ solution of [CuCl(dppet)(mftztH)] with one additional equivalent of the same thione ligand produced a new product causing the replacement of the chlorine atom by the thione. In the new halogene-free product (compound **14**, Scheme 4), one of the thione units was found to be coordinated in its thiolate form as a consequence of deprotonation. It should be noted that this type of coordination has been previously observed in the case of $[Cu(PPh_3)_2(bztzdtH)(bztzdt)]$ [20] which was formed under similar experimental conditions. This thiolate coordination – due to a spontaneous HX elimination of unknown origin – has occurred, apparently, in only a few cases and it is a very interesting phenomenon which needs to be investigated further.

The analogous reaction of copper(I) iodide, carried out under the same conditions as for the monomerics of general formula [CuX(dppet)L], always gave the thione-free dimeric compound $[CuI(dppet)]_2$ which contains double-bridging iodine atoms. Furthermore, an interesting exception was observed for the reaction between copper(I) iodide, dppet and pymtH. The latter, carried out under the same experimental conditions as usual, proceeded in a unique way (Scheme 5) to give crystals which were found to contain two totally different thione-free molecules, namely the dimeric complex $[CuI(dppet)]_2$ (compound **13a**) and also the monomer $[CuI(CH_3CN)(dppet)]$ (compound **13b**). In light of the pronounced tendency of copper(I) iodide mixed ligand complexes toward dimerization [2], the formation of the former dimer [Cu(μ-I)(dppet)] was not surprising, however,it was fully unexpected for the soft Cu(I) to form the later monomeric compound because of its preference for the soft sulphur of the thione over the harder nitrogen base of acetonitrile.

The above variety of products seemed to be indicative of the lability of the coordinated dppet and this prompted us to investigate the possibility of substitution of the chelated diphosphine. When a threefold excess of triphenylphosphine ($PPh_3$) was refluxed with [CuX(dppet)L] in acetonitrile/methanol mixture, or in acetone, the products obtained were of the formula $[CuX(PPh_3)_2L]$.



Scheme 4.



Scheme 5.

On the contrary, no substitution was observed when the dimers $[CuX\{\mu\text{-}S(pymtH)\}(pymtH)]_2$ were treated under similar conditions. Likewise, the mixture of $[CuI(dppet)]_2$ and $[CuI(CH_3CN)(dppet)]$ (compound **13**) could not be forced to undergo any alterations, e.g., when treated with triphenylphosphine or with excess of a thione at the temperature of refluxing acetone or THF.

All prepared complexes are coloured, diamagnetic, air stable, microcrystalline solids that are moderately soluble in acetonitrile and only marginally soluble in chloroform and acetone. The composition of the compounds has been confirmed by elemental analysis. Their solutions in acetone and chloroform are non-conducting.

### *3.2. Spectroscopy*

The electronic absorption spectra of the complexes in chloroform solutions appear to be mainly of intraligand character, presenting two broad bands with maxima in the 243–255 and 280–310 nm regions, respectively. The first one can be attributed to intraligand $\pi^* \leftarrow \pi$ transitions on the phenyl group of the phosphine ligand, since the uncoordinated *cis*-1,2-bis(diphenylphosphino) ethylene reveals a strong absorption at 258 nm which usually remain unshifted upon coordination to Cu(I). 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 be, therefore, considered as a thione-originating intraligand transition which possess some MLCT character [21,22]. The infrared spectra of compounds **1**–**14**, recorded in the range 4000–250 $cm^{-1}$show all the expected strong phosphine bands, which remain practically unshifted upon coordination. Moreover, the spectra of compounds under investigation contain, with the exception of that of the iodo-compounds (**12**, **13**), all of the bands required by the presence of the heterocyclic thione ligands. In detail, they exhibit the usual four "thioamide bands" in the regions ~ 1510, 1320, 1000 and 750 $cm^{-1}$, although in some cases partly masked by strong phosphine absorptions, as well as the characteristic NH stretching vibrations observed in the ~3150 $cm^{-1}$region. The shifts observed for these bands due to coordination in combination with the lack of $\nu$(SH) bands at ca. 2500–2600 $cm^{-1}$, signify the exclusive S-coordination mode of the thione ligands. Because of poor solubility in the common deuterated solvents, the NMR study of the prepared complexes is unfortunately incomplete. For the most soluble, however, $^1$H NMR spectra were recorded in deuterated chloroform and displayed the signals expected for the phosphine and thione ligands, as well as a single broad resonance at ~11–14 ppm attributed to the NH proton reflecting the prevailance of the thione tautomer in the complexes.

### *3.3. Description of the structures*

The X-ray crystal structures of complexes **9**, **14**, **13a**, **13b** and **16** (details of crystal and structure refinement are shown in Table 1) have been determined. The common structural feature of all five compounds is the tetrahedral coordination of the copper(I), whereas compounds **9**, **13a, 13b** and **16** contain the diphosphine unit coordinated in the expected chelating fashion.

#### *3.3.1. [CuBr(dppet)(mftztH)] (9)*

Main bond lengths and angles for compound **9** are given in Table 2, and a perspective drawing showing the atom numbering is shown in Fig. 1.

In the monomeric complex copper(I) exhibits a highly distorted tetrahedral co-ordination geometry, with the metal atom being surrounded by two P, one S and one bromine atoms. The largest deviation from the ideal geometry is reflected by the P(1)–Cu(1)–P(2) and P(1)–Cu(1)–Br(1) angles whose values of 91.45(3)° and 127.00(2)°, respectively, are markedly different than the tetrahedral value of 109.4°. The first angle corresponds to the bite angle of the rigid chelating phosphane ligand and should be considered as quite normal but the second one is unexpected large, much larger than the two P–Cu–S angles including the sterically bulky thione ligand. These structural parameters contrast with those of some monomeric copper(I) bromide complexes which contain one heterocyclic thione and two monodentate triphenylphosphane ligands, exhibiting the same $CuSP_2Br$ core but also with the structure of [CuBr(dppp)(pymtH)] [12] containing the non-rigid 1,2-propanebis(diphenylphosphine). The CuPCCP five-membered ring is twisted about the Cu(1)–P(2) bond adopting a half-chair conformation with deviations of 0.2073 and −0.1955 Å for Cu(1) and P(2), respectively, from the plane defined by P(1), C(5) and C(6). As a consequence of the lack of coplanarity within the chelate ring no significant π bonding interaction should be expected throughout the coordination plane and the ethene bridge, a fact that is further indicated by the aliphatic double bond length of

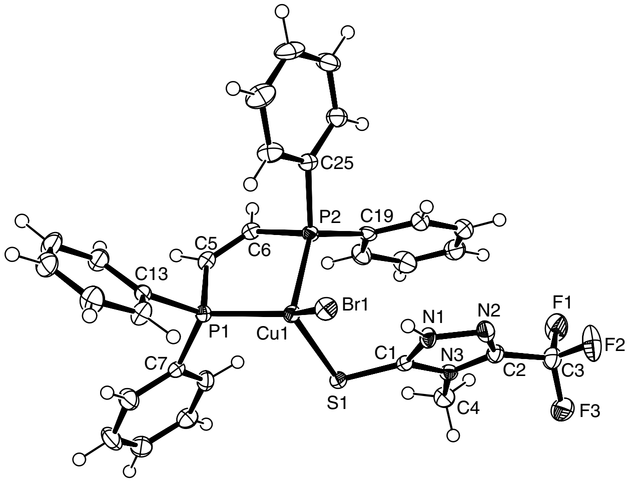


Fig. 1. A view of compound **9** with atom labels. Displacement ellipsoids are shown in the 50% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for **9**

| | | | |
|---|---|---|---|
| Cu(1)–Br(1) | 2.4118 (4) | P(1)–C(7) | 1.828 (3) |
| Cu(1)–P(1) | 2.2302 (7) | P(1)–C(5) | 1.830 (3) |
| Cu(1)–P(2) | 2.2893 (7) | P(2)–C(6) | 1.824 (3) |
| Cu(1)–S(1) | 2.3495 (7) | C(5)–C(6) | 1.331 (4) |
| S(1)–C(1) | 1.685 (3) | P(2)–C(19) | 1.815 (3) |
| P(1)–C(13) | 1.824 (2) | P(2)–C(25) | 1.835 (3) |
| P(1)–Cu(1)–P(2) | 91.45(3) | Cu(7)–P(1)–Cu(1) | 122.19 (9) |
| P(1)–Cu(1)–S(1) | 106.15(3) | C(5)–P(1)–Cu(1) | 102.39(9) |
| P(2)–Cu(1)–S(1) | 102.03(2) | C(19)–P(2)–C(6) | 104.51(12) |
| P(1)–Cu(1)–Br(1) | 127.00(2) | C(19)–P(2)–C(25) | 105.55(12) |
| P(2)–Cu(1)–Br(1) | 111.51(2) | C(6)–P(2)–C (25) | 99.86(12) |
| S(1)–Cu(1)–Br(1) | 114.00(2) | C(19)–P(2)–Cu(1) | 118.74(8) |
| C(1)–S(1)–Cu(1) | 99.72 (8) | C(6)–P(2)–Cu(1) | 100.90(8) |
| C(13)–P(1)–C(7) | 104.41(11) | C(25)–P(2)–Cu(1) | 123.56(8) |
| C(13)–P(1)–C(5) | 105.25(11) | C(6)–C(5)–P(1) | 121.6(2) |
| C(7)–P(1)–C(5) | 98.40(11) | C(5)–C(6)–P(2) | 121.1(2) |
| C(13)–P(1)–Cu(1) | 120.50(8) | | |

1.331(4) Å which remains practically unchanged upon chelation [23].

An additional striking feature of the present structure is the Cu(1)–S(1)–C(1) angle of 99.78(8)° which is the smallest one observed among the thione-S coordinated copper(I) complexes structurally characterized by us so far and can be associated with the presence of a strong hydrogen bond between the halogen and the N(1)H. Because of their extraordinary inequality, which may be considered as rather unusual for a chelating diphosphane, the two individual Cu–P distances of 2.2302(7)° and 2.2893(7)° are placed in the lower and upper limit respectively of the value range expected for tetrahedrally coordinated Cu(I). Moreover, the planes of the two aromatic rings of each $PPh_2$ moiety are essentially perpendicular to one another. Within the heterocyclic thione ligand which exhibits a strictly planar five-membered ring, the bond distances and angles are not altered significantly upon coordination. Finally, the Cu–S and Cu–Br bond lengths lie in the range normally observed for tetrahedrally coordinated copper(I) complexes with terminal bromine and thione–sulphur donors.

### 3.3.2. *[Cu(dppet)(mftztH)(mftzt)] (**14**)*

Main bond lengths and angles are listed in Table 3, and a view of the structure showing the atom numbering appears in Fig. 2. The four-coordinate monomer reveals a copper coordination sphere consisting of two P atoms of one dppet and two S atoms from two mftztH ligands. In connection with the above discussed structure for **9**, there exist a few marked differences, which should be commended upon, since they emerge from the substitution of the halogen by a thione ligand.

Comparison of the CuPCCP framework of the two complexes shows the slightly reduced P–Cu–P angle of 90.25(5)° in **14** (vs. 91.45(3)° in **9**) which could be considered as obviously closer to the ideal bite angle of the phosphine ligand since it is associated with the formation of an almost planar five-membered chelate ring. The copper, the P(1) atom and the ethene bridge are nearly coplanar and the deviations from least-sqares plane througt the following atoms are as follows: Cu(1), 0.0008; P(1), −0.0015; C(9), 0.0022; C(10), −0.0014; P(2), −0.1448 Å.

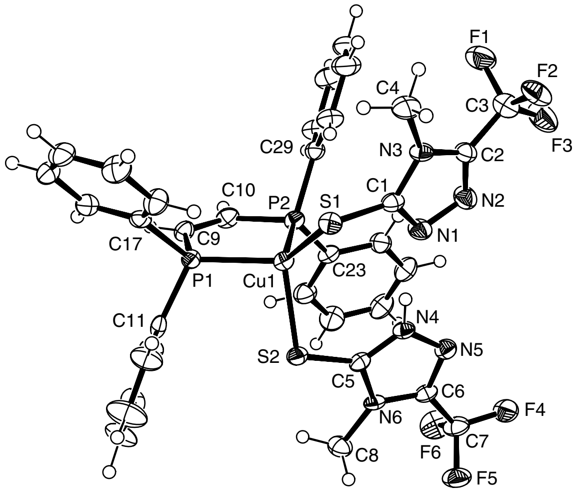


Fig. 2. A view of compound **14** with atom labels. Displacement ellipsoids are shown in the 50% probability level.

In accordance to that later fact the C–C double bond length of 1.325(6) Å is slightly shorter compared to the value of 1.334(4) Å observed for the free phosphine [24], probably as a result of partial charge delocalization throughout the chelate ring. These more "regular" conditions are additionally reflected in the values of the two individual Cu–P distances (2.2541(14)° and 2.2682(15)°), which are nearly equal against their remarkable inequality within the structure of **9**.

Table 3
Selected bond lengths (Å) and angles (°) for **14**

| | | | |
|---|---|---|---|
| Cu(1)–P(1) | 2.2541(14) | P(1)–C(11) | 1.827(5) |
| Cu(1)–P(2) | 2.2682(15) | P(1)–C(9) | 1.830(5) |
| Cu(1)–S(1) | 2.2947(14) | P(1)–C(17) | 1.833(5) |
| Cu(1)–S(2) | 2.3538(14) | P(2)–C(10) | 1.819(5) |
| S(1)–C(1) | 1.716(5) | P(2)–C(23) | 1.829(5) |
| S(2)–C(5) | 1.690(5) | P(2)–C(29) | 1.843(5) |
| C(9)–C(10) | 1.325(6) | | |
| P(1)–Cu(1)–P(2) | 90.25(5) | C(11)–P(1)–Cu(1) | 115.14(14) |
| P(1)–Cu(1)–S(1) | 123.50(5) | C(9)–P(1)–Cu(1) | 104.45(16) |
| P(2)–Cu(1)–S(1) | 118.61(5) | C(17)–P(1)–Cu(1) | 124.20(16) |
| P(1)–Cu(1)–S(2) | 98.06(5) | C(10)–P(2)–C(23) | 102.1(2) |
| P(2)–Cu(1)–S(2) | 106.03(5) | C(10)–P(2)–C(29) | 100.6(2) |
| S(1)–Cu(1)–S(2) | 115.90(5) | C(23)–P(2)–C(29) | 102.6(2) |
| C(1)–S(1)–Cu(1) | 101.24(17) | C(10)–P(2)–Cu(1) | 102.90(16) |
| C(5)–S(2)–Cu(1) | 107.40(16) | C(23)–P(2)–Cu(1) | 120.17(14) |
| C(11)–P(1)–C(9) | 101.7(2) | C(29)–P(2)–Cu(1) | 124.43(16) |
| C(11)–P(1)–C(17) | 103.9(2) | C(10)–C(9)–P(1) | 119.3(4) |
| C(9)–P(1)–C(17) | 104.9(2) | C(9)–C(10)–P(2) | 122.7(4) |

Interestingly, the C–S bonds but also the adjacent C–N bonds of both thione molecules do not differ significantly, retaining most of their double bond character, despite the deprotonation in one of these units. On the other hand the deprotonated thione ligand is bonded to the metal center with the "short" Cu(1)–S(1) bond distance of 2.2947(14) Å which is comparable with the value of 2.302(4) Å observed for $[\mathrm{CuBr(py2SH)(PPh_3)_2}]$ [24] bearing the heterocyclic thione ligand also in its deprotonated form, whereby the neutral thione unit participates in the significantly longer Cu(1)–S(2) bond distance of (2.3538(14) Å) which is usual for tetrahedrally coordinated copper(I) and compares well with the one observed in **9**. An additional striking feature of this structure is the one-sided inclination of the two five-membered triazoline-rings which are twisted with respect to each other to be nearly coplanar. This orientation further contributes to the distortions of the tetrahedral geometry around copper(I) and should be attributed to the presence of a strong hydrogen bond [N(4)–H(4)···N(1); N(4)–H(4) = 0.8804 Å, H(4)···N(1) = 1.8572 Å, N(4)···N(1) = 2.726(5) Å, N(4)–H(4)···N(1) = 168.62°].

### *3.3.3. [Cu(μ-I)(dppet)]₂ (**13a**) and [CuI(dppet)(CH₃CN)] (**13b**)*

The title compounds **13a** and **13b** co-crystallize in the monoclinic space group $P2_1/c$ with eight discrete molecules (four of each) in the unit cell. Selected bond lengths and angles for compounds **13a** and **13b** are given in Tables 4 and 5 and respective drawings showing the atom numbering are shown in Figs. 3 and 4, respectively. Both molecules possess no crystallographically imposed symmetry.

In the dimeric complex **13a**, the two copper(I) centers are joined by two iodine bridges to form a four-membered $\mathrm{Cu_2I_2}$ core with a Cu···Cu separation of 3.0144(7) Å which is too long to invoke any appreciable metal–metal interaction. The strongly distorted tetrahedral coordination around each copper(I) central atom is completed by the two P donor atoms of the chelating dppet unit. The tendency of copper(I) iodide to form dimeric complexes with two iodine atoms serving as bridges between the two copper atoms is already well established and can be attributed to its strong preference to be ligated from soft donors such as iodine. Thus, among the structures of mixed-ligand copper(I) halide complexes containing tertiary arylphosphines and heterocyclic thiones characterized by us so far, dimeric species with a $\mathrm{Cu(\mu\text{-}I)_2PS}$ core are quite common, whereas in the presence of the harder chlorine dimerization have been achieved via the softer thione-S donor atom.

Moreover, we recently observed this tendency to be accompanied with an additional interesting effect, namely the exclusion of the thione ligand from the coordination sphere, when a bidentate phosphine ligand such as 1,3-propanebis(diphenylphosphine) (dppp) or 1,5-pentanebis(diphenylphosphine) (dpppe) is used instead of the simple monodentate arylphosphines. The same type of behaviour is once more observed in the present structure, which displays an additional quite unexpected feature namely a remarkable non-planarity within the $\mathrm{Cu_2I_2}$ central core. Unlike in the analogous dimeric complex $[\mathrm{Cu(\mu\text{-}I)(dppp)}]_2$[dppp = 1.3-propanebis(diphenylphosphine)] with a strictly planar $\mathrm{Cu_2I_2}$ core, in the structure under investigation the two main planes through I(1), Cu(1), I(2) and I(1), Cu(2), I(2) form a dihedral angle of 139.16(2)°, with I(2) being displaced from the mean plane defined by Cu(1), I(1) and Cu(2) by 1.0788(7) Å. It seems likely that this remarkable feature stems from crystal packing effects. Moreover, within the $\mathrm{Cu_2I_2}$ backbone, there are four

Table 4
Selected bond lengths (Å) and angles (°) for **13a**

| | | | |
|---|---|---|---|
| Cu(1)–I(1) | 2.6658 (5) | Cu(2)–P(4) | 2.2805 (11) |
| Cu(1)–I(2) | 2.6063 (5) | P(1)–C(49) | 1.813 (4) |
| Cu(2)–I(2) | 2.6380 (5) | C(49)–C(50) | 1.337 (6) |
| Cu(2)–I(1) | 2.6087 (5) | C(50)–P(2) | 1.829 (4) |
| Cu(1)–P(1) | 2.2752 (11) | P(3)–C(51) | 1.829 (4) |
| Cu(1)–P(2) | 2.2704 (11) | C(51)–C(52) | 1.328 (5) |
| Cu(2)–P(3) | 2.2843 (11) | C(52)–P(4) | 1.828 (4) |
| Cu(1)–Cu(2) | 3.0144(7) | | |
| Cu(1)–I(1)–Cu(2) | 69.701(15) | P(4)–Cu(2)–I(2) | 115.79 (3) |
| Cu(2)–I(2)–Cu(1) | 70.169(15) | P(3)–Cu(2)–I(2) | 110.55(3) |
| P(1)–Cu(1)–P(2) | 90.44(4) | I(1)–Cu(2)–I(2) | 104.959(18) |
| P(2)–Cu(1)–I(2) | 121.40(3) | C(49)–P(1)–Cu(1) | 103.38(13) |
| P(1)–Cu(1)–I(2) | 122.18(3) | C(50)–P(2)–Cu (1) | 103.22(14) |
| P(2)–Cu(1)–I(1) | 113.78(3) | C(51)–P(3)–Cu(2) | 102.67(13) |
| P(1)–Cu(1)–I(1) | 103.81(3) | C(52)–P(4)–Cu(2) | 102.22(13) |
| I(2)–Cu(1)–I(1) | 104.236(18) | C(50)–C(49)–P(1) | 121.5(3) |
| P(4)–Cu(2)–P(3) | 90.43(4) | C(49)–C(50)–P(2) | 121.0(3) |
| P(4)–Cu(2)–I(1) | 116.74(3) | C(52)–C(51)–P(3) | 120.8(3) |
| P(3)–Cu(2)–I(1) | 118.42(3) | C(51)–C(52)–P(4) | 122.3(3) |

Table 5
Selected bond lengths (Å) and angles (°) for **13b**

| | | | |
|---|---|---|---|
| Cu(3)–P(5) | 2.2829 (12) | P(5)–C(77) | 1.824 (4) |
| Cu(3)–P(6) | 2.2670 (11) | P(6)–C(78) | 1.823 (4) |
| Cu(3)–N(1) | 2.014 (3) | C(77)–C(78) | 1.332 (6) |
| Cu(3)–I(3) | 2.5993 (6) | C(79)–C(80) | 1.454 (5) |
| N(1)–C(79) | 1.132 (5) | | |
| N(1)–Cu(3)–P(5) | 112.86(11) | C(77)–P(5)–Cu(3) | 102.66(14) |
| N(1)–Cu(3)–P(6) | 119.20(10) | C(78)–P(6)–Cu(3) | 103.43(13) |
| P(6)–Cu(3)–P(5) | 88.84(4) | C(78)–C(77)–P(5) | 120.7(3) |
| P(5)–Cu(3)–I(3) | 119.26(3) | C(77)–C(78)–P(6) | 120.3(3) |
| P(6)–Cu(3)–I(3) | 113.81(3) | Cu(3)–N(1)–C(79) | 166.9(4) |
| N(1)–Cu(3)–I(3) | 103.49(10) | N(1)–C(79)–C(80) | 175.5(5) |

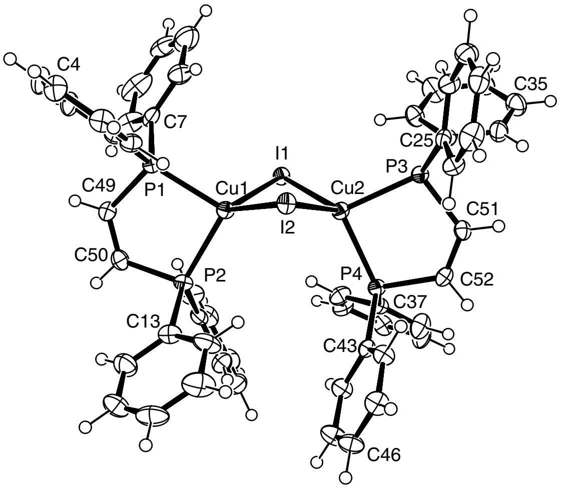


Fig. 3. A view of compound **13a** with atom labels. Displacement ellipsoids are shown in the 50% probability level.

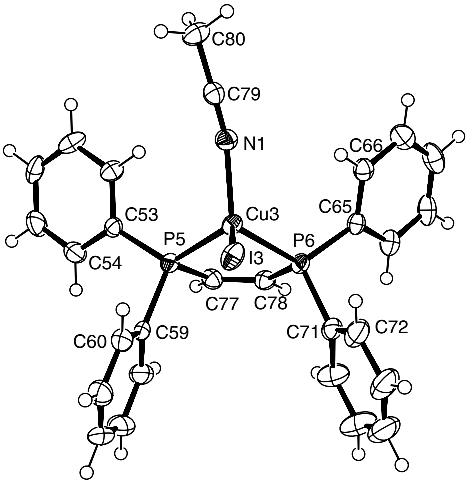


Fig. 4. A view of compound **13b** with atom labels. Displacement ellipsoids are shown in the 50% probability level.

clearly different Cu–I bond distances lying in the range 2.6063(5)–2.6658(5) Å which are somewhat shorter than the corresponding bond distances observed in bis[μ-iodo(pyridine-2-thione)(tri-m-tolylphosphine)copper(I)] [5].

The two five-membered chelate rings are ordered almost parallel to each other including an angle of only 4.0°. The double bond lengths within the two ethene bridges are somewhat different (1.337(6) and 1.328(5) Å, respectively). Interestingtly, the former value, being somewhat longer than the ideal aliphatic double bond length, corresponds to the almost planar chelate ring formed by Cu(1), P(1), C(49), C(50) and P(2) whereby the second distingtly distorted ring contains the shorter aliphatic bond. Thus these aliphatic double bond values hardly can be connected with the presence of any essential π bonding interaction throughout the five-membered $P_2C_2Cu$ arrangements. The four individual Cu–P bonds lie in the narrow range 2.2704(11)–2.2843(11) Å and are very similar to those observed in [Cu(dppet)$_2$]PF$_6$ [23] and also in other copper(I) diphosphine complexes having a tetrahedral structure, e.g., in [Cu(μ-I)(dppp)]$_2$.

The bite angles of the two phosphane ligands (90.44(4)° and 90.43(4)°, respectively) are well below what is ideal for a tetrahedrally coordinated metal ion but very close to the intraligand P–Cu–P values of 89.69(7)° and 89.90(7)° observed in the above-mentioned [Cu(dppet)$_2$]PF$_6$.

In complex **13b**, copper(I) exhibits a highly distorted tetrahedral coordination geometry, with the metal atom being surrounded by two P, one I, and one N donor atoms. A particularly striking feature of this structure is the coordination of the hard base nitrogen even in the presence of a thione containing the soft base sulphur. The largest deviation from the ideal geometry is reflected by the P(5)–Cu(3)–057P(6) angle whose value of 88.84 (4)° is markedly lower than the tetrahedral value of 109.4°.

It is interesting to note that for a series of tetrahedraly coordinated copper(I) halide complexes which contain two monodentate triphenylphosphine ligands, the largest angle was found, as expected, between the two most bulky phosphine ligands. In the complex under investigation, however, the chelating dppet ligand is bonded to the copper(I) center with an acute bite angle which is even somewhat smaller than the corresponding P–Cu–P bite angles in complex **13a**. This lower angle is counterbalanced by an appropriate expansion of the two angles P(5)–Cu(3)–I(3) and N(1)–Cu(3)–P(6) whose values of 119.26 (3)° and 119.20 (10)° are clearly larger than the tetrahedral angle.

The inequality of the two Cu–P bonds whose values are 2.28.29 (12) and 2.26.70 (11) Å is somewhat larger than in complex **13a**. Moreover, these values are shorter than those found in $[Cu(dppp)_2]BF_4$ [25] or in other monomeric copper(I) complexes with chelating diphosphines, e.g., in $[Cu(dppe)_2]ClO_4$. Finally, the Cu–I and Cu–N bond lengths lie in the range normally observed for tetrahedrally coordinated copper(I) complexes with terminal iodine and nitrogen donors.

### 3.3.4. *[CuBr{μ-S(pymtH)}(pymtH)]₂ (**16**)*

Main bond lengths and angles are given in Table 6 and an ORTEP view of molecule **16** showing the atom numbering scheme is given in Fig. 5. The basic structural unit of [CuBr{μ-S(pymtH)(pymtH)]₂ is a dimer in which the two copper atoms, separated by 2.7409(9) Å, are doubly bridged by two S atoms of the thione ligands to form a strictly planar four-membered $Cu_2S_2$ core. The highly distorted tetrahedral coordination around each copper is completed by the S atom of a terminally bonded pyrimidine-2-thione ligand and one bromine atom. Each of the two *trans*-positioned bromine atoms stabilize the complex with two strong intramolecular hydrogen bonds [N(1)···Br(1) = 3.598(3) Å, H(1)···Br(1) = 2.7406 Å, N(1)–H(1)···Br(1) = 164.85° and [N(3)···Br(1) = 3.311(3) Å, H(3)···Br(1) = 2.4372 Å, N(3)–H(3)···Br(1) = 172.02°]. atom. Each of the two *trans*-positioned bromine atoms stabilize the complex with two strong intramolecular hydrogen bonds [N(1)···Br(1) = 3.598(3) Å, H(1)···Br(1) = 2.7406 Å, N(1)–H(1)···Br(1) = 164.85° and [N(3)···Br(1) = 3.311(3) Å, H(3)···Br(1) = 2.4372 Å, N(3)–H(3)···Br(1) = 172.02°].

Each of the two inequivalent Cu–S bonds of 2.5634(10) and 2.2727(9) Å are within the range expected for binuclear Cu(I) complexes with double bridging sulfur atoms but the marked feature of the present structure is the extremly large asymmetry in the two bridging distances. By comparison, these distances are 2.444(1) and 2.386(2) Å in bis[μ-S(benzimidazoline-2-thione)(tmtp)copper(I)chloride] (tmtp = tri-m-tolylphosphine) and 2.4879(7) and 2.3348(9) Å in bis[μ-S(pyridine-2-thione)(tmtp)copper(I)bromide].

The two terminally bonded bulky thione ligands are *trans*-disposed with a Cu–S bond distance of 2.2776(10) Å, which is equal to the "short" one in the Cu–S–Cu bridge and thus significantly shorter than the values normaly observed for the terminal Cu–S bond of tetrahedraly coordinated copper(I) complexes. The Cu–Br bond distance of 2.4556(5) Å lies between the values observed in the two above-mentioned dimeric copper(I) bromide compounds with double bridging sulphur atoms, thus confirming the previously observed association of this bond length with the S–Cu–S angle. In fact, an elongation of the Cu–Br bond results as a consequence of the opening up of the S–Cu–S angle and the shortening of the Cu···Cu separation. Finally, the S–Cu–S and Cu–S–Cu angles of 111.25(3)° and 68.75(3)°, respectively, are close to the ideal values (109.5° and 70.5°) predicted for symmetric dimers.

## 3.4. *Computational study*

Searching for the factors which determine the local metal environment in monovalent copper coordination compounds, one can suggest that, besides steric effects, the Lewis basicity of the ligands should be of major importance. However, in view of the remarkable variety of structures obtained within the closely related series of thione ligands used in the past but also in this work, additional considerations are required in order to explain the formation of the energetically favorable geometry in each particular case. The computations performed in the present paper are an attempt to explore the possibility of electronic factors in affecting the chemical and structural behaviour of the above-mentioned compounds.

Table 6
Selected bond lengths (Å) and angles (°) for **16**

| | | | |
|---|---|---|---|
| Cu(1)–S(2)#1 | 2.2727(9) | Cu(1)–Cu(1)#1 | 2.7409(9) |
| Cu(1)–S(1) | 2.2776(10) | S(1)–C(1) | 1.697(3) |
| Cu(1)–Br(1) | 2.4556(5) | S(2)–C(5) | 1.707(3) |
| Cu(1)–S(2) | 2.5634(10) | S(2)–Cu(1)#1 | 2.2727(9) |
| S(2)#1–Cu(1)–S(1) | 105.76(4) | S(1)–Cu(1)–Br(1) | 121.01(3) |
| S(2)#1–Cu(1)–Br(1) | 119.65(3) | S(2)#1–Cu(1)–S(2) | 111.25(3) |
| S(1)–Cu(1)–S(2) | 102.55(3) | C(1)–S(1)–Cu(1) | 106.22(13) |
| Br(1)–Cu(1)–S(2) | 94.41(3) | S(2)–Cu(1)–Cu(1)#1 | 50.60(2) |
| S(2)#1–Cu(1)–Cu(1)#1 | 60.65(3) | C(5)–S(2)–Cu(1)#1 | 110.71(12) |
| S(1)–Cu(1)–Cu(1)#1 | 115.37(3) | C(5)–S(2)–Cu(1) | 107.80(12) |
| Br(1)–Cu(1)–Cu(1)#1 | 118.82(3) | Cu(1)#1–S(2)–Cu(1) | 68.75(3) |

#1 Symmetry transformation $-x+2, -y, -z$ used to generate equivalent atoms.

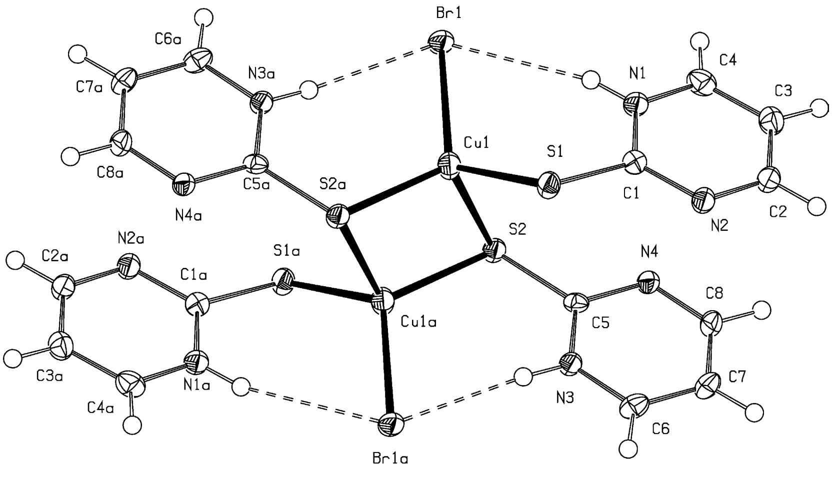


Fig. 5. A view of compound **16** with atom labels. Displacement ellipsoids are shown in the 50% probability level.

As menthioned above, there is an unusual bend of the $Cu_2I_2$ central core in compound **13a** which may be attributed to crystal packing effects. To examine whether it is true, calculations were made on two model structures (**I** and **II**) constructed on the basis of the prototype compound by altering only the positional parameters of the atoms within the $Cu_2I_2$ framework in such a way that a strictly planar centrosymmetric moiety is being formed in each case, keeping the rest of the molecule unchanged (Fig. 6).

In both model structures, the same Cu(1)–I(1) bond distance, taken as the mean value of the experimentally observed Cu(1)–I(1) and Cu(2)–I(2) distances, as well as the same Cu(1)–I(2) bond distance, equal to the mean value of the experimentally observed Cu(1)–I(2) and Cu(2)–I(1) ones, were used. Model structure **I** was chosen to display I–Cu–I angles equal to the mean value observed in the original structure to keep the distortions at a minimum with respect to the overal geometry around the two copper(I) centers, which are now separated by 3.216 Å (against the value of 3.014 Å in the real molecule). On the other hand, maintaining the Cu–I–Cu angles intact, therefore increasing the separation between the two bulkier iodine atoms, produces the more realistic model structure **II** in which the Cu···Cu separation remains unaffected.

The calculated overlap populations between the two metal centers, which are separated by 3.0144(7) Å, are 0.005 e and 0.004 e for the "real" dimeric structure **13a** and the model structure **II** respectively. In both cases the bonding nature of these metal–metal interactions is of negligible importance to the formation of the dimeric structure. Besides, the stabilizing effect of a metal–metal interaction could be important for Cu···Cu separations below the value of 2.80 Å proposed to be the sum of two copper van der Waals radii. Thus, the corresponding overlap population of 0.015 e calculated for the rather short Cu···Cu distance of 2.7409(9) Å in $[CuBr\{\mu\text{-}S(pymtH\}(pymtH)]_2$ (**16**), may be an evidence for such a stabilization. Nevertheless, it is of interest to notice that for the given Cu···Cu separation of 3.0144(7) Å the calculated copper–copper interaction loses slightly in bonding character on going from the "real" molecule to the planar model structure **II**, but this fact hardly can be considered as a factor contributing to the bending of the $Cu_2I_2$ central core in complex **13a**. The least favourable structure relative to this aspect is, however, model structure **I** in which the interaction between the considerably withdrawed copper atoms becomes, as expected, antibonding in character (−0.001 e). Moreover, the HOMO–LUMO gap of 2.081 eV in the true structure remains practicaly constant in the two model structures (2.056 and 2.057 eV for **I** and **II**, respectively), as a consequence of the fact that no orbitals belonging to copper or iodine atoms do participate in these two frontier orbitals. Thus, it remains unclear whether the structures bearing a planar $Cu_2I_2$ central core could be energeticaly more favourable with regard to the "real" one.

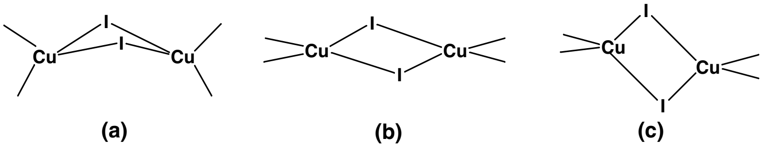


Fig. 6. Sketches of the $Cu_2I_2$ core: (a) side view of the real molecule, (b) top view of model I, (c) top view of model II.

The calculated overlap populations for the Cu(1)–I(1) and Cu(1)–I(2) bonds in **13a** are 0.244 e and 0.315 e, respectively. Upon coordination the Cu(I) metal center accepts electron density from both the iodide and the phosphine ligands. Considering these particular bonds, several interesting facts can be noticed. Each of the two Cu(I) centers acquires a slightly differed net charge with the difference being greater in the two model structures bearing the planar $C_2I_2$-moieties. The sum of the computed bond overlap populations of the four individual Cu–I bonds bonds drops slightly on going from the ‘‘real’’ molecule to the any of the model structures. The same holds true also for the total overlap population of the four Cu–P bonds. For each of the two chelate rings in the ‘‘real’’ molecule, the calculated overlap populations of the individual Cu–P bonds, ranging between 0.534 and 0.546 e, are much closer to each other as in the two model structures, illustrating the bend conformation of the $C_2I_2$-core to allow a better copper–phosphine interaction. Thus, electronic effects are likely to be causal for the bend structure adopted by molecule **13a**.

Considering the energetic conditions in the two cocrystallized complexes **13a** and **13b**, the lowest unoccupied molecular orbitals (LUMO) for **13a** and **13b** are 2.081 and 3.442 eV, respectively, higher than their highest occupied molecular orbitals (HOMO). This large difference in the HOMO–LUMO gaps of the two complexes clearly indicates the monomeric compound to be more stable than its dimeric counterpart and may be essential in view of the simultaneous formation of the two species.

## 4. Conclusions

The coordination capability of the rigid diphosphane *cis*-1,2-bis(diphenylphosphino) ethylene (dppet) toward Cu(I) halides in the presence of heterocyclic thione donor groups has been studied. Continuing our investigations on the factors governing the stereochemical preferences of copper(I) compounds, we were primary interested in preparing complexes bearing dppet as a chelating ligand. Indeed, dppet was found to adopt the desired coordination mode in all the new complexes, but this was the only common feature among the diverse structures that occurred as a result of reaction stoichiometries and conditions chosen. Thus, the well-known extraordinary flexibility of Cu(I) was once more displayed during the present investigation in a fascinating manner. In particular, according to previous observations, treating an acetonitrile suspension of copper(I) chloride or bromide with stoichiometric amounts of methanolic solutions of dppet and a heterocyclic thione ligand, the complexes formed at ambient temperature were of the formula [CuX(dppet)L], whereby the thione-free dimer $[Cu(\mu\text{-}I)(dppet)]_2$ was the main product of the analogous reaction when copper(I) iodide was used. Working at higher temperatures, however, copper(I) chloride and bromide clearly showed preference for the soft sulphur donor forming pseudo-tetrahedral dimerics with the thione ligand adopting both the bridging and the terminal coordination mode, as we were able to demonstrate in the case of pyrimidine-2-thione. Among the structures obtained in the course of the present work particular attention belongs to that of [Cu(dppet)(mftztH)(mftzt)] derived from [CuCl(dppet)(mftztH)], since it contains the second thione unit coordinated in the thiolate form. Given that such a thiolate coordination takes place under spontaneous HX elimination which is apparently of unknown origin, this very interesting phenomenon needs further extensive examination.

As for the two thione-free molecules **13a** and **13b**, formation of the dimer $[Cu(\mu\text{-}I)(dppet)]_2$ was by no means unexpected, given the well established strong tendency of copper(I) iodide to form halo-bridged dimers, in some cases even under exclusion of the thione ligand from the coordination sphere. In the second one, $[CuI(dppet)(CH_3CN)]$, however, the coordination of the hard donor nitrogen, instead of the soft sulphur of the thione present, despite Cu(I) being soft and thiophillic, should be considered as rather strange. Nevertheless, a question related to the simultaneous formation of these two species still remains to be answered. Finally, extended Hückel calculations provide some evidence for electronic interactions to be responsible for the uncommon non-planarity adopted by the $Cu_2I_2$ moiety in $[Cu(\mu\text{-}I)(dppet)]_2$.

## 5. Supplementary material

CCDC-211226 (9), CCDC-211224 (14), CCDC-211223 (13) and CCDC-211225 (16) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.code.cam.ace.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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