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# Study of mixed ligand copper(I) complexes with tri-*m*-tolylphosphine (tmtp) and heterocyclic thiones. Crystal structures of bis[$\mu$-S(benzimidazoline-2-thione)(tmtp) copper(I) chloride] and bis[$\mu$-Br(thiazolidine-2-thione)(tmtp) copper(I)]

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## Abstract

Reactions of $[Cu(tmtp)X]_n$ (tmtp = tri-*m*-tolyl-phosphine; X = Cl, Br) with heterocyclic thiones (L) (L = pyridine-2-thione (py2SH), pyrimidine-2-thione (pymtH), 1,3-thiazolidine-2-thione (tzdtH), 1-methyl-1,3-imidazoline-2-thione (meimtH), benz-1,3-imidazoline-2-thione (bzimtH$_2$) and quinoline-2-thione (qntH)) yield binuclear complexes of the general formula $[Cu(tmtp)(L)X]_2$. The complexes have been characterized by elemental analyses and their IR, UV–Vis and $^1$H NMR spectroscopic data. The photolysis of these complexes in dichloromethane solutions has been investigated. The crystal structures of $[Cu(tmtp)(bzimtH_2)Cl]_2$ (**I**) and $[Cu(tmtp)(tzdtH)Br]_2$ (**II**) have been determined by single-crystal X-ray diffraction methods. The white crystals of the two compounds are both monoclinic, space group $P2_1/a$ with $a = 12.636(8)$, $b = 15.325(6)$, $c = 13.696(8)$ Å, $\beta = 102.76(3)°$, $D_{calc} = 1.421(1)$ Mg m$^{-3}$, $V = 2586.5(3)$ Å$^3$ and $Z = 2$ for $[Cu(tmtp)(bzimtH_2)Cl]_2$ and space group $P2_1/n$ with $a = 15.085(1)$, $b = 9.820(3)$, $c = 17.263(1)$ Å, $\beta = 99.77(3)°$, $D_{calc} = 1.494$ Mg m$^{-3}$, $V = 2520.2(4)$ Å$^3$ and $Z = 2$ for $[Cu(tmtp)(thzdtH)Br]_2$. The chloro complex contains a planar $Cu_2S_2$ moiety with Cu–S bond lengths of 2.386(2) and 2.444(1) Å and Cu–P and Cu–Cl distances equal to 2.251(1) and 2.391(2) Å, respectively. The Cu···Cu separation is 2.764(1) Å. The bromo molecule forms a planar $Cu_2Br_2$ frame with Cu–Br bond lengths of 2.5182(2) and 2.5971(8) Å and Cu–P and Cu–S distances equal to 2.240(1) and 2.307(1) Å, respectively. The Cu···Cu separation is 3.3471(7) Å. Rationalization of the above described properties in terms of stereoelectronic factors governing bond formation is attempted by means of EHT computations.

## Introduction

Copper(I) complexes are continuously investigated mainly because of Cu(I) involvement in certain biochemical redox reactions [1]. Small molecular weight Cu(I) compounds with the metal coordinated to sulfur and nitrogen are used as models for the study of chemical and physicochemical interactions involving the real macromolecules *in vivo*. An interesting feature of Cu(I) in such compounds is its tendency to acquire a pseudo-four-coordinated geometry by forming dimer compounds; these have also attracted considerable interest since they offer additionally the possibility of studying metal–metal interactions between d$^{10}$ metal centers [2, 3]. Along this line a vast amount of dimeric adducts with heterocyclic thione as ligands have been structurally characterized [4–8].

We believe the heterocyclic thiones represent more accurately the thioamido moieties present in the vicinity of copper within biological media. In a sequence of studies [9–13] we have investigated the synthesis, photoreactivity and structural analysis of several such dimers, namely $[Cu(PPh_3)(py2SH)Br]_2$ [9], $[Cu(tptp)(pymtH)Cl]_2$ [10], $[Cu(tptp)(tzdH)Cl]_2$, [11] (complexes **III**, **IV** and **V** hereafter) and $[Cu(tmtp)(py2SH)I]_2$ [12] where tptp = tri-*p*-tolylphosphine. Several synthetic routes have been applied in the above effort owing to the diversity of binding of the triarylphosphines used. The present study aims at the completion of our research on the vast series of the above-mentioned mixed ligand compounds; we hereby report on the synthesis, characterization, pho-

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**I** L = bzimtH, P = tmtp, X = Cl
**II** L = thzdtH, P = tmtp, X = Br
**III** L = py2SH, P = $PPh_3$, X = Br
**IV** L = pymtH, P = tptp, X = Cl
**V** L = tzdH, P = tptp, X = Cl

Fig. 1. Molecular structure of the studied and related dimer complexes. Ligand notation as in text.

tochemical and computational study of a new series of complexes of the general formula $[Cu(tmtp)(L)X]_2$ where X = Cl, Br; L = py2SH, pymtH, tzdtH, meimtH, $bzimtH_2$ and qntH (Fig. 1).

## Experimental

### *Materials and instruments*

All solvents used were of reagent grade. Copper halides and tmtp (Merck) were used as obtained, while the thiones (Merck or Aldrich) were recrystallized from hot ethanol prior to their use.

IR, electronic and NMR spectra, conductivities, magnetic suceptibility measurements and elemental analyses of C, N and H were performed as described previously [10].

The photolyses and quantum yields measurements were carried out in 1 cm quartz cells to which light emitted from a high pressure HBO 200W/4 Osram lamp was directed through a 2 cm water filter and an 'Applied Photophysics' monochromator. All the photochemical work was carried out in dark.

### *Preparation of the complexes*

$[Cu(tmtp)X]_n$ which served as starting materials for the synthesis of the studied complexes were prepared by heating equimolar quantities of CuX and tmtp at 50–70 °C in acetonitrile, for about 30 min.

The complexes of the formula $[Cu(tmtp)(L)X]_2$, were prepared according to the following general procedure. A solution of 0.1 mmol of the appropriate thione in 20 ml of methanol was added to a solution of $[Cu(tmtp)X]_n$ (in the ratio 1:1 with CuX) in 20 ml acetonitrile and the resulting solution was moderately heated for 30 min. It was then allowed to cool and the microcrystalline products were isolated. The compounds were identified by elemental analyses and by their IR, UV–Vis and NMR spectra. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of $[Cu(tmtp)(tzdtH)Br]_2$ and $[Cu(tmtp)(bzimtH)Cl]_2$ in acetonitrile.

### *Computational details*

The calculations were performed using the EHT Hamiltonian [14] as implemented in the ICON8 program [15]. Owing to the size of the molecules under investigation as well as to the comparative nature of the study, the calculations were performed on suitable models; the thione molecules were represented by $H_2C{=}S$ moieties while $PMe_3$ was substituted for the bulky tri-*m*-tolylphosphine. In both cases a strict symmetry ($sp^2$ around thione C and $sp^3$ around P and phosphine C) was adopted. The chloro compounds **1** were built up on the observed $Cu_2S_2$ core of $[Cu(tmtp)(bzimtH)Cl]_2$, adopting the mean Cu–Cl and Cu–P distances [10, 11, 16] in a series of related complexes. The bromo compounds **2** were also constructed similarly on the observed $Cu_2Br_2$ backbone using Cu–S and Cu–P distances [4, 9] from the corresponding compounds whose crystal structure has been reported. The $\mu$-S-bromo compound models **3** were set up on the existing $Cu_2S_2$ core of the chloro ones and the corresponding Cu–Br and Cu–P lengths which were used were derived as previously mentioned (Fig. 2).

The EHT parameters, i.e. $H_{ii}$ and $\zeta_i$, for Cu, P and halogen atoms were those established in the literature, while for S and C, the parameters were obtained from iterative calculations on the thione ligands. In this respect, the electronic effect of each thione molecule is induced into the model compound, while the phosphine effect is kept constant and the steric hinderance originating from either ligand minimized.

### *Solution of the structures*

Suitable crystals of the complex were obtained from a slow evaporation of a methanol–acetonitrile (1:1) solution at room temperature. Crystallographic data and details of data collection and refinement are listed in Table 1. Data reduction was performed by the Enraf-Nonius SDP/VAX [17] package; Lorentz and polarization effects were corrected. An absorption correction was applied by $\Psi$ scan of the reflections $\bar{1}1\bar{1}$, $\bar{2}2\bar{2}$, $\bar{3}3\bar{2}$, $\bar{3}4\bar{2}$ with minimum and maximum reflection transmissions 0.96 and 0.99, respectively, for $[Cu(tmtp)(bzimtH)Cl]_2$; an analogous one of the reflection $\bar{1}\bar{2}0$, $\bar{2}\bar{3}0$, $\bar{2}\bar{4}\bar{1}$ and $\bar{3}\bar{4}\bar{1}$ with minimum and maximum reflection transmissions 0.856 and 0.999 for $[Cu(tmtp)(tzdtH)Br]_2$. In the latter case intensities were

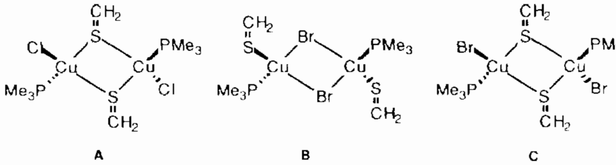

Fig. 2. Model compounds used in the calculations.

TABLE 1. Crystal structure data for $[Cu(tmtp)(tzdtH)Br]_2$ and $[Cu(tmtp)(bzimtH_2)Cl]_2$

| | | |
|---|---|---|
| Formula | $Cu_2Br_2S_4P_2N_2C_{48}H_{52}$ | $Cu_2Cl_2S_2P_2N_2C_{56}H_{54}$ |
| Formula weight | 1134.06 | 1107.14 |
| $a$ (Å) | 15.085(1) | 12.636(8) |
| $b$ (Å) | 9.820(3) | 15.325(6) |
| $c$ (Å) | 17.263(1) | 13.696(8) |
| $\beta$ (°) | 99.77(3) | 102.76(3) |
| $V$ (Å$^3$) | 2520.2(4) | 2586.5(3) |
| $D_{calc}$ (Mg m$^{-3}$) | 1.494 | 1.421(1) |
| $Z$ | 2 | 2 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/a$ |
| Crystal size (mm) | 0.4×0.3×0.2 | 0.1×0.14×0.28 |
| Linear absorption coefficient (cm$^{-1}$) | 26.72 | 11.07 |
| $F$(000) | 1152 | 1144 |
| Diffractometer | Enraf-Nonius-CAD4F | Enraf-Nonius-CAD4F |
| Radiation | Mo K$\alpha$ ($\lambda=0.71073$)<br>graphite-monochromator | Mo K$\alpha$ ($\lambda=0.71073$)<br>graphite-monochromator |
| Temperature (K) | 296(1) | 297(1) |
| $\theta_{min}$, $\theta_{max}$ (°) for cell determination | 7, 17 | 7, 17 |
| No. reflections for cell determination | 25 | 25 |
| $\theta_{min}$, $\theta_{max}$ | 2, 25 | 2, 25 |
| $\omega/2\theta$ scan (°) | $\Delta\omega$ 0.80+0.35 tan $\theta$ | $\Delta\omega$ 0.80+0.35 tan $\theta$ |
| $hkl$ limits | $0\rightarrow17$, $0\rightarrow11$, $-20\rightarrow20$ | $0\rightarrow17$, $0\rightarrow11$, $-20\rightarrow20$ |
| Reflections measured | 4902 | 4955 |
| Reflections observed with $I>3\sigma(I)$ | 3011 | 2698 |
| No. refined parameters | 301 | 325 |
| Quantity minimized $\Sigma w\|\|F_o\|-\|F_c\|\|^2$ | $1/w=\sigma^2(F_o)+0.0003\|F_o\|^2$ | $1/w=\sigma^2(F_o)+0.0004\|F_o\|^2$ |
| $R$, $R_w$ | 0.03, 0.03 | 0.039, 0.038 |
| Max. parameter shift, $(\Delta/\sigma)_{max}$ | 0.03 (C23, $y$) | −0.084 (C11, $y$) |

rescaled for decay (0.5%) on the base of intensity reduction of standard reflections.

The structures were solved by direct methods, SHELX-86 [18]. Copper scattering factors and analogous dispersion values were from the International Tables for Crystallography [19]. For other atoms the scattering factors were those included in the SHELX-77 program [20]. The H-atom coordinates were calculated on stereochemical grounds. They were refined on the constraints of the pivot carbon atoms. Only the H atoms attached to the N atoms were determined from difference Fourier synthesis. The structure was refined by full-matrix least-squares methods [20]: non-H atoms were refined anisotropically and H atoms were refined with individual isotropic thermal parameters. The only exceptions were the fixed thermal parameters of hydrogen atoms of methyl groups in the tmtp moieties and hydrogen atoms attached to the C18 (phenyl ring of tmtp) and C24 (thiazolidine ring) in $[Cu(tmtp)(tzdtH)Br]_2$. N–H bond distances were adjusted to the theoretical values. Interatomic distances, calculated bond and torsion angles and preparation of drawings were performed by the EUCLID package [21] and programs and plots of the molecules by the ORTEP program [22].

All crystallographic calculations were carried out on the MICROVAXII computer in the X-ray Laboratory of Rudjer Boskovic Institute, Zagreb, Croatia, Yugoslavia.

## Results and discussion

All the complexes are microcrystalline solids soluble in chloroform, acetonitrile, ethanol, methanol and acetone. The elemental analyses confirm their stoichiometry and their physical properties are in accordance with the proposed structures (see Table 2). Room temperature magnetic measurements on several species confirmed the diamagnetic nature of the compounds.

### *Spectroscopic study*

The UV–Vis spectra of the complexes were recorded in dichloromethane as described previously and are dominated by two main absorptions in the regions 250–260 and 280–310 nm, respectively. The first band is ascribed to the intraligand (IL) transitions of the phosphine ligand for which one band is observed at 260 nm having log $\epsilon$ values (*c.* 4.1) similar to their counterparts in the complexes. The second band expresses a small red shift (10–20 nm) with respect to the corresponding one in the spectra of the free thiones and is ascribed to metal to ligand charge transfer transition (MLCT).

TABLE 2. Analytical data and some relevant physical properties of the complexes

| Complex | $\Phi$ | Colour | Melting point (°C) | Elemental analysis: found (calc.) (%) | | |
|---|---|---|---|---|---|---|
| | | | | C | H | N |
| $[Cu(tmtp)(py2SH)Br]_2$ | 0.013 | orange | 145 | 54.40(55.82) | 4.56(4.65) | 2.90(2.50) |
| $[Cu(tmtp)(py2SH)Cl]_2$ | 0.024 | orange | 142 | 61.64(60.64) | 5.25(5.05) | 2.88(2.72) |
| $[Cu(tmtp)(pymtH)Br]_2$ | 0.195 | red | 148 | 53.12(53.57) | 4.35(4.46) | 4.79(5.00) |
| $[Cu(tmtp)(pymtH)Cl]_2$ | 0.081 | red | 154 | 58.28(58.19) | 4.70(4.85) | 5.22(5.43) |
| $[Cu(tmtp)(qntH)Br]_2$ | 0.021 | red | 148 | 59.14(59.11) | 4.67(4.60) | 2.39(2.30) |
| $[Cu(tmtp)(qntH)Cl]_2$ | 0.038 | red | 158 | 63.21(63.76) | 4.92(4.96) | 2.59(2.48) |
| $[Cu(tmtp)(tztdH)Br]_2$ | 0.085 | pale yellow | 140 | 51.02(50.79) | 4.76(4.59) | 2.57(2.47) |
| $[Cu(tmtp)(tztdH)Cl]_2$ | 0.095 | pale yellow | 155 | 55.02(55.11) | 4.99(4.98) | 2.92(2.69) |
| $[Cu(tmtp)(meimtH)Br]_2$ | 0.208 | white | 155 | 52.88(53.38) | 4.73(4.80) | 4.82(4.98) |
| $[Cu(tmtp)(meimtH)Cl]_2$ | 0.167 | white | 162 | 57.58(57.97) | 5.17(5.22) | 5.66(5.41) |
| $[Cu(tmtp)(bzimtH_2)Br]_2$ | 0.275 | white | 160 | 58.15(56.38) | 4.38(4.19) | 4.51(4.70) |
| $[Cu(tmtp)(bzimtH_2)Cl]_2$ | 0.111 | white | 173 | 60.74(60.92) | 4.76(4.53) | 4.97(5.08) |

Note should be made at this point that coordinated phosphine molecules and halogen atoms cause shifts of the MLCT bands to lower [23] and higher [24] wavelengths, respectively.

IR spectra recorded in the region 4000–250 cm$^{-1}$ provide information concerning the coordination mode of the ligands, since they reveal the dominance of the thione form of the ligands investigated deduced by the presence of $\nu$(NH) bands at 3200–3130 cm$^{-1}$ [25], the absence of any evidence for $\nu$(SH) bands in the 2500–2600 cm$^{-1}$ [26] region and the presence of characteristic 'thioamide bands' [26] as well as the characteristic medium $\nu$(Cu–S) bands at 370–340 cm$^{-1}$ [27].

The $^1$H NMR spectra of the compounds in $CDCl_3$ solution at ambient temperature display, apart from the signals expected for the phosphine and thione ligands, a single resonance at $\delta$ ~11–14 ppm attributed to the NH protons, thus confirming the prevalence of the thione tautomer in the complexes.

## *Crystal structure determination*

### *[Cu(tmtp)(bzimtH$_2$)Cl]$_2$ (I)*

Final atomic coordinates of the non–H atoms and their isotropic equivalent thermal parameters, and bond lengths and angles are presented in Tables 3 and 4, respectively. The molecular structure and packing in the unit cell are depicted in Figs. 3 and 4, respectively. In the dimeric complex each of the copper(I) atoms displays a distorted tetrahedral environment formed by one P atom from tmtp, one Cl atom and two inequivalent bridging S atoms from the thione ligand. All the atoms in the $Cu_2S_2$ core are strictly coplanar. The two *trans* positioned chlorine atoms stabilize the complex with two intramolecular hydrogen bonds (N2···Cl = 3.084(4) Å, H···Cl = 2.105(4) Å and N–H–Cl = 162(2)°).

The five-membered ring of the thione ligand is planar (max. deviation: 0.041 Å for C22). The Cu–S bond distances of 2.444(1) and 2.386(2) Å lie within the range expected for binuclear Cu(I) complexes with double bridging sulfur atoms. The remarkable asymmetry in the two bridging Cu–S distances has also been

TABLE 3. Cartesian coordinates and equivalent thermal parameters for the non-hydrogen atoms of $[Cu(tmtp)(bzimtH)Cl]_2$

| Atom | $x$ | $y$ | $z$ | $U^a$ |
|---|---|---|---|---|
| Cu | 0.0595(0) | 0.5298(0) | 0.0909(0) | 362(2) |
| P | 0.0490(1) | 0.5147(1) | 0.2520(1) | 299(4) |
| S | −0.0995(1) | 0.6012(1) | −0.0121(1) | 343(4) |
| Cl | 0.1788(1) | 0.6459(1) | 0.0697(1) | 427(4) |
| N1 | −0.2760(3) | 0.6416(3) | 0.0621(3) | 348(14) |
| N2 | −0.2457(3) | 0.5018(2) | 0.0578(3) | 349(14) |
| C(1) | −0.0436(3) | 0.5941(3) | 0.2864(3) | 273(14) |
| C(2) | −0.1348(4) | 0.5731(3) | 0.3235(3) | 325(17) |
| C(3) | −0.2071(4) | 0.6377(3) | 0.3404(3) | 367(19) |
| C(4) | −0.1859(4) | 0.7235(3) | 0.3207(3) | 422(21) |
| C(5) | −0.0942(4) | 0.7449(4) | 0.2848(4) | 483(20) |
| C(6) | −0.0245(4) | 0.6816(3) | 0.2676(3) | 395(19) |
| C(7) | −0.3048(4) | 0.6150(4) | 0.3812(4) | 578(23) |
| C(8) | 0.0066(4) | 0.4104(3) | 0.2966(3) | 315(16) |
| C(9) | −0.0614(4) | 0.3579(3) | 0.2292(4) | 414(18) |
| C(10) | −0.1019(4) | 0.2798(3) | 0.2589(4) | 483(20) |
| C(11) | −0.0685(4) | 0.2546(3) | 0.3573(4) | 482(20) |
| C(12) | 0.0018(4) | 0.3055(4) | 0.4246(4) | 483(20) |
| C(13) | 0.0383(4) | 0.3843(3) | 0.3951(3) | 405(18) |
| C(14) | −0.1826(6) | 0.2268(4) | 0.1852(5) | 886(31) |
| C(15) | 0.1789(3) | 0.5381(3) | 0.3380(3) | 320(14) |
| C(16) | 0.1881(4) | 0.5779(3) | 0.4304(3) | 355(18) |
| C(17) | 0.2896(4) | 0.5939(3) | 0.4926(3) | 403(18) |
| C(18) | 0.3815(4) | 0.5686(3) | 0.4602(4) | 429(19) |
| C(19) | 0.3723(4) | 0.5295(4) | 0.3685(4) | 480(20) |
| C(20) | 0.2721(4) | 0.5135(3) | 0.3067(3) | 384(18) |
| C(21) | 0.2984(4) | 0.6373(4) | 0.5930(4) | 602(24) |
| C(22) | −0.2088(4) | 0.5802(3) | 0.0388(3) | 315(17) |
| C(23) | −0.3608(4) | 0.6014(3) | 0.0937(3) | 360(17) |
| C(24) | −0.4540(4) | 0.6335(4) | 0.1174(4) | 494(21) |
| C(25) | −0.5257(5) | 0.5736(4) | 0.1402(4) | 603(25) |
| C(26) | −0.5040(5) | 0.4845(5) | 0.1425(4) | 621(25) |
| C(27) | −0.4110(4) | 0.4511(4) | 0.1181(4) | 523(24) |
| C(28) | −0.3414(4) | 0.5121(3) | 0.0927(3) | 366(16) |

$^aU_{eq} = (U_{11} + U_{22} + U_{33})/3$.

TABLE 4. Intramolecular bond lengths (Å) and angles (°) for $[Cu(tmtp)(bzimtH)Cl]_2$

| | | | |
|---|---|---|---|
| Bond lengths | | | |
| Cu-S | 2.444(1) | C3-C7 | 1.504(8) |
| Cu-S' | 2.386(2) | C10-C14 | 1.505(8) |
| Cu-P | 2.251(1) | C17-C21 | 1.509(7) |
| Cu-Cl | 2.391(2) | S1-C22 | 1.709(5) |
| Cu-Cu | 2.764(1) | C22-N1 | 1.352(7) |
| P-C1 | 1.821(5) | N1-C23 | 1.386(7) |
| P-C8 | 1.833(5) | C23-C28 | 1.391(7) |
| P-C15 | 1.832(4) | C28-N2 | 1.404(7) |
| <C-C> sp$^2$ | 1.386(7) | N2-C22 | 1.335(6) |
| Angles | | | |
| Cl-Cu-S | 93.3(1) | C2-C3-C7 | 121.1(4) |
| P-Cu-S | 113.1(1) | C4-C3-C7 | 120.2(4) |
| P-Cu-Cl | 111.8(1) | C9-C10-C14 | 120.3(5) |
| S-Cu-S' | 110.2(1) | C11-C10-C14 | 121.4(5) |
| P-Cu-S' | 114.9(1) | C16-C17-C21 | 120.4(4) |
| S'-Cu-Cl | 111.7(1) | C18-C17-C21 | 121.1(5) |
| Cu-P-C1 | 111.4(1) | Cu-S-C22 | 108.4(2) |
| Cu-P-C8 | 120.1(1) | Cu'-S-C22 | 107.3(2) |
| Cu-P-C15 | 111.8(2) | N2-C22-N1 | 108.4(4) |
| C1-P-C8 | 104.2(2) | N2-C28-C23 | 106.3(4) |
| C1-P-C15 | 103.8(2) | C22-N2-C28 | 109.2(4) |
| C8-P-C15 | 104.1(2) | C28-C23-N1 | 106.5(4) |
| <C-C-C> sp$^2$ | 119.9(5) | C23-N1-C22 | 109.5(4) |

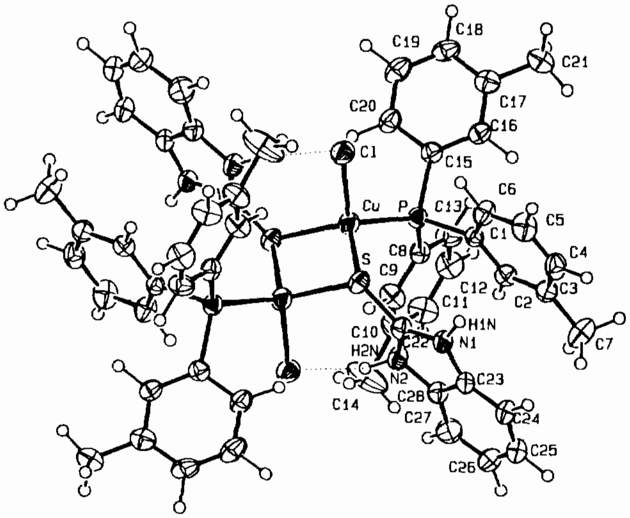

Fig. 3. Structure of $[Cu(tmtp)(bzimtH)Cl]_2$. Dashed lines denote N-H···S hydrogen bonds.

observed before in similar complexes as in the case of **IV** and **V** [10, 11] (see Fig. 1), however the reason for this asymmetry is not yet obvious.

The Cu-P bond distance of 2.251(1) Å is the largest one observed in analogous dimeric complexes with sulfur or halogen atoms as bridging coordinating groups, only slightly shorter than the corresponding one in monomeric tetrahedral Cu(I) complexes [9-12].

Contrary to the above observation, the Cu-Cl bond distance of 2.391(2) Å is the longest Cu-Cl bond observed so far in Cu(I) dimers. It is noteworthy that this metal-halogen bond distance is associated with the S-Cu-S angle. The relationship can be nicely demonstrated by comparing **I** with **IV** and **V** which have been studied recently [10, 11]. In fact, an opening up of the S-Cu-S angle in **V** (93.24(2)° against 92.48(2)° in **IV**) results in an elongation of the Cu-Cl bond (2.300(1) and 2.283(1) Å in **IV** and **V**, respectively). The effect is more marked in **I**, where the S-Cu-S angle is widened to 110.2(1)° provoking a significant elongation of the Cu-Cl bond. On the other hand a good linear correlation appears to exist between the Cu-Cl bond distance and the Cu···Cu separation in the three compared complexes. As the Cu···Cu contact becomes shorter (3.359(1) Å in **V**, 3.316(0) Å in **IV** and 2.764(1) Å in **I**), the Cu-Cl distances gains in magnitude, so we propose that electronic rather than steric factors affect the Cu-Cl bond length. However this phenomenon needs more detailed examination in consideration of further structures of this series.

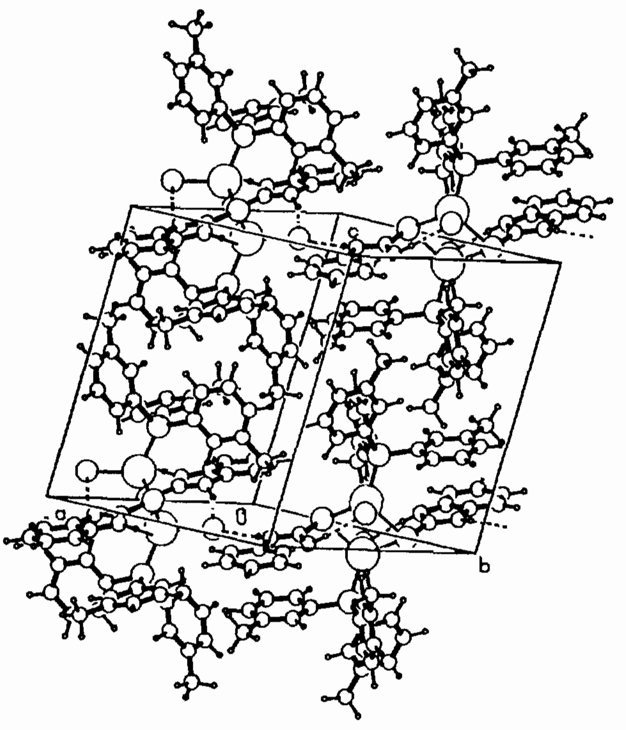

Fig. 4. A view of the monoclinic unit cell $[Cu(tmtp)(bzimt)Cl]_2$. Dashed lines denote N-H···S hydrogen bonds.

Unlike in the previous complexes **IV** and **V**, the S-Cu-S and Cu-S-Cu angles (110.2(1) and 69.8(1)°) are very close to the ideal values (109.5 and 70.5°) for symmetric dimers. There exist some other differences between the angles of the three compared complexes; so the Cl-Cu-P angle of 111.8(1) in **I** is somewhat smaller than the corresponding value in **IV** and **V** (119.7(0) and 119.5(0)°, respectively). Moreover, the

S–Cu–Cl angle in **IV** and **V** is not far from the tetrahedral value (110.0(0) and 112.5(0)°, respectively), whereas the same angle in **I** is significantly distorted (93.3(1)°).

### *[Cu(tmtp)(tzdtH)Br]₂ (II)*

Final atomic coordinates of the non-H atoms and their isotropic equivalent thermal parameters, and bond lengths and angles are presented in Tables 5 and 6, respectively. The molecular structure and packing in the unit cell are depicted in Figs. 5 and 6, respectively. The dimeric complex has a crystallographic symmetry centre. The double bridging bromine atoms generate a strictly planar $Cu_2Br_2$ core, in which both of the copper(I) atoms have identically distorted tetrahedral environments with a Cu···Cu distance of 3.3471(7) Å. The other two positions of each tetrahedron are occupied by a P atom of tri-*m*-tolyl-phosphine and a S atom of thiazolidine-2-thione.

The Cu–Br bond distances of 2.5182(2) and 2.5971(8) Å are comparable with the values of 2.571(1) and 2.589(1) Å found in $[Cu(P^tBu_3)Br]_4$ [28] apart from the asymmetry in the bridge, which is remarkable larger in the present complex. By comparison with other mixed ligand CuBr complexes containing phosphines and heterocyclic thiones, the bridging Cu–Br bond distances are generally longer than those found in monomeric compounds with tetrahedral [9] or trigonal [29] coordination around copper, as well as in dimeric ones with double bridging sulfur atoms.

TABLE 5. Cartesian coordinates and equivalent thermal parameters of the non-hydrogen atoms of $[Cu(tmtp)(tzdtH)Br]_2$

| Atom | $x$ | $y$ | $z$ | $U^a$ |
|---|---|---|---|---|
| Br | 0.0076(0) | 0.1199(0) | 0.0898(0) | 418(1) |
| Cu | 0.0871(0) | 0.0841(1) | −0.0256(0) | 426(2) |
| P | 0.2338(1) | 0.0352(1) | 0.0066(1) | 339(3) |
| S1 | 0.0556(1) | 0.2546(1) | −0.1181(1) | 621(5) |
| S2 | −0.0679(1) | 0.4869(1) | −0.1663(1) | 758(6) |
| N1 | −0.0714(2) | 0.3512(4) | −0.0427(2) | 540(15) |
| C(1) | 0.2701(2) | −0.0818(4) | 0.0855(2) | 366(12) |
| C(2) | 0.3556(2) | −0.1390(4) | 0.1030(2) | 409(14) |
| C(3) | 0.3829(3) | −0.2226(4) | 0.1678(2) | 488(17) |
| C(4) | 0.3221(3) | −0.2526(4) | 0.2168(2) | 581(19) |
| C(5) | 0.2367(3) | −0.1963(4) | 0.2027(2) | 606(17) |
| C(6) | 0.2104(3) | −0.1104(4) | 0.1391(2) | 478(16) |
| C(7) | 0.4790(3) | −0.2740(5) | 0.1861(3) | 71(20) |
| C(8) | 0.2882(2) | −0.0345(3) | −0.714(2) | 344(12) |
| C(9) | 0.2394(2) | −0.1242(4) | −0.1247(2) | 499(14) |
| C(10) | 0.2773(3) | −0.1858(5) | −0.1837(2) | 584(17) |
| C(11) | 0.3653(3) | −0.1548(5) | −0.1893(3) | 636(19) |
| C(12) | 0.4148(3) | −0.0656(5) | −0.1373(3) | 643(19) |
| C(13) | 0.3766(2) | −0.0037(4) | −0.0788(2) | 500(15) |
| C(14) | 0.2234(4) | −0.2831(6) | −0.2401(3) | 979(27) |
| C(15) | 0.3001(2) | 0.1900(4) | 0.0345(2) | 419(12) |
| C(16) | 0.2967(3) | 0.2916(4) | −0.0221(3) | 553(18) |
| C(17) | 0.3449(3) | 0.4113(4) | −0.0073(3) | 687(22) |
| C(18) | 0.3961(4) | 0.4294(5) | 0.0659(3) | 846(27) |
| C(19) | 0.3987(3) | 0.3309(5) | 0.1238(3) | 789(22) |
| C(20) | 0.3513(3) | 0.2100(4) | 0.1080(2) | 549(18) |
| C(21) | 0.3411(4) | 0.5196(5) | −0.0694(4) | 1158(34) |
| C(22) | −0.0286(3) | 0.3586(4) | −0.1020(2) | 464(16) |
| C(23) | −0.1469(4) | 0.4440(6) | −0.0405(4) | 675(22) |
| C(24) | −0.1483(4) | 0.5435(6) | −0.1073(4) | 785(24) |

[a] $U_{eq} = (U_{11} + U_{22} + U_{23})/3$.

TABLE 6. Intramolecular bond lengths (Å) and angles (°) for $[Cu(tmtp)(tzdtH)Br]_2$

| | | | |
|---|---|---|---|
| Bond lengths | | | |
| Cu–Br | 2.5182(2) | C3–C7 | 1.517(6) |
| Cu–Br′ | 2.5971(8) | C10–C14 | 1.501(7) |
| Cu–P | 2.240(1) | C17–C21 | 1.504(7) |
| Cu–S1 | 2.307(1) | S1–C22 | 1.679(5) |
| Cu–Cu | 3.3471(7) | C22–N1 | 1.301(5) |
| P–C1 | 1.832(4) | N1–C23 | 1.464(7) |
| P–C8 | 1.825(4) | C24–S2 | 1.799(7) |
| P–C15 | 1.838(4) | S2–C22 | 1.730(4) |
| $<C–C>sp^2$ | 1.386(6) | | |
| Angles | | | |
| Br–Cu–Si | 112.12(5) | C4–C3–C7 | 120.8(4) |
| P–Cu–S1 | 113.96(6) | C9–C10–C14 | 120.5(4) |
| P–Cu–Br | 112.90(5) | C11–C10–C14 | 121.1(4) |
| Br–Cu–Br | 98.28(2) | C16–C17–C21 | 120.9(5) |
| P–Cu–Br | 114.62(4) | C18–C17–C21 | 120.7(4) |
| Br′–Cu–S1 | 103.34(4) | Cu–S1–C22 | 113.1(1) |
| P–Cu–C15 | 111.0(1) | S1–C22–N1 | 126.6(3) |
| C15–P–C8 | 102.2(2) | S1–C22–S2 | 121.5(3) |
| C8–P–C1 | 102.8(2) | S2–C22–N1 | 112.0(3) |
| C1–P–Cu | 118.6(1) | C22–N1–C23 | 119.1(4) |
| C15–P–C1 | 103.8(2) | N1–C23–C24 | 107.1(5) |
| Cu–P–C8 | 116.5(1) | C23–C24–S2 | 108.0(4) |
| $<C–C–C>sp^2$ | 120.0(4) | C24–S2–C22 | 93.2(3) |
| C2–C3–C7 | 120.4(3) | | |

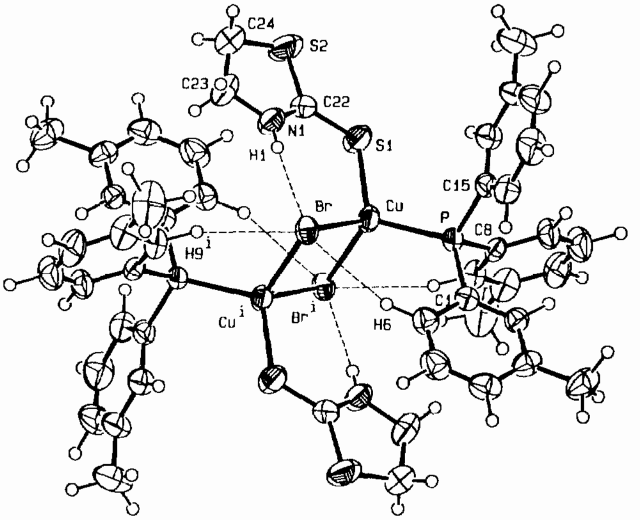

Fig. 5. Structure of $[Cu(tmtp)(tzdtH)Br]_2$. Dashed lines denote N–H···Br hydrogen bonds.

The Cu–S bond length of 2.307(1) Å is in the range of that observed in the trigonal planar complex [Cu(totp)(tzdtH)Br] [29] (2.290(1) Å) while it lies rather

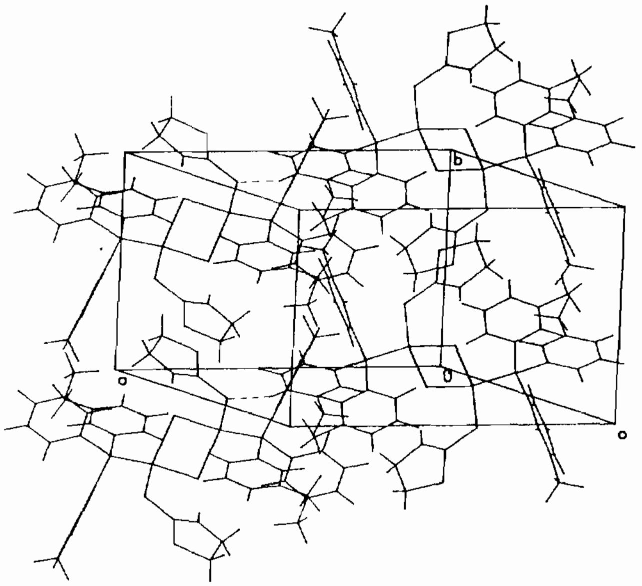

Fig. 6. A view of the monoclinic unit cell [Cu(tmtp)(tzdtH)Br]$_2$. Dashed lines denote N–H···S hydrogen bonds.

near the lower limit of tetrahedral Cu(I) complexes [9, 30]. These suggest that coordination number, ligand type and size only slightly affect the Cu–S bond distance.

The two bulky tmtp ligands are *trans* disposed with a Cu–P bond distance of 2.240(1) Å. This value is exactly the same observed in [Cu(tmtp)(py2SH)I]$_2$ [12], where halogen atoms also act as double-bridging ligands. In **III** and **IV** [9, 10], where the thione sulfur atoms form the bridges, the corresponding values are 2.227(1) and 2.308(0) Å, respectively.

Moreover, by comparing the Cu–P bond distances for Cu(I) complexes containing triphenyl- or tritolylphosphine and heterocyclic thiones as ligands, we see in general the larger values for the triphenylphosphine compounds. Thus, the differences in this bond distance can be connected, in all probability, with electronic effects on the part of the phosphine ligand.

The C–H···Br intramolecular interactions (C···Br = 3.783(4) Å for C6–H···Br and 3.874(3) Å for C9–H··· Br) stabilize the complex and reduce the flexibility of the *m*-tritolylphosphine ligands.

The dihedral angle between the Cu, Br, Cu$^i$, Br$^i$ and Cu, S1, Cu$^i$, S1$^i$ planes is 83.22(4)°. Each of the two thiazolidine rings and the adjacent copper atoms are nearly planar (largest deviation for Cu = 0.074(11) Å). Due to intramolecular hydrogen bonding N1–H···Br(N···Br = 3.299(4) Å, H···Br = 2.49(4) Å and <N–H–Br = 171(4)°) the six-membered ring formed by H1, N1, C22, S1, Cu and Br is planar as well (max. deviation: 0.10 Å for the Cu atom). Bond angles involving the bulky *m*-tritolylphosphine ligands are more open, but the largest deviation from the tetrahedral angle is the small angle of 98.8(2)° for Br$^i$–Cu–Br.

The Br–Cu–Br and Cu–Br–Cu angles (98.28(2) and 81.72(2)°) deviate from the ideal values for symmetric dimers, reflecting the distortions induced by the hydrogen contacts, but are close to the ideal geometry for $Y_2MX_2MY_2$ dimers according to theoretically proposed criteria [31].

### *Photochemical study*

Irradiation of the complexes in dichloromethane solutions at $\lambda_{exit} = 300$ nm at room temperature causes the decomposition of the complexes within minutes, without the evolution of new bands in the UV–Vis spectra. The decomposition of the complexes is not at all unexpected on the grounds of the lability of the triphenylphosphine ligand in solution [10–13, 32].

Quantum yields have been determined at room temperature relative to potassium ferroxalate standard and are reported in Table 2.

### *Computational study*

The rather short Cu···Cu distances, especially for [Cu(bzimtH$_2$)(tmtp)Cl]$_2$ observed in the above complexes prompted us to undertake a computational study in order to verify the origin and possible consequences as well as to unravel the factors leading to the $\mu$-S and $\mu$-Br dimer formation in the chloro and bromo compounds, respectively. The details of the approximations and parameters used are reported in the computational section of 'experimental'.

A general observation is that the FMOs of the model compounds are mainly of thione origin as their population analysis proves; in a few instances, the bromo compounds possess a significant Br contribution to their LUMO as well, while only in the 'thiazolidine-thione' model are the FMOs constituted mainly of phosphine orbitals.

In all the cases the Cu···Cu interaction is negligible [33], the overall overlap population between the two metal atoms being slightly bonding in the case of the chloro compounds and slightly antibonding in the bromo compounds, the latter being certainly of higher magnitude than the former, though not exceeding 0.012 e. The individual values of this overlap are quite close in each group of compounds, therefore inhibiting direct correlation of the thione-induced electronic effect to the overall electron distribution of the dimers.

Another point of interest is the computational evidence for the experimentally observed oxidation of copper(I) chlorides, relative to the stability of their bromide counterparts; the FMO energetic differences between the two classes of compounds argue for the enhanced dative ability of the chlorides HOMO, since they lie generally about 2.5 eV higher than the HOMO of the corresponding bromides. The slight differences in the HOMO–LUMO values computed account for the small shift of the lower energy visible bands in the two classes of compounds and they point to a mixed intraligand and MLCT combined with partial LL'CT character of these bands.

Since the preference of the $\mu$-S structure (Fig. 2, **A**) in the chloro compounds contradicts the one for $\mu$-Br in the corresponding bromides (Fig. 2, **B**), a further study was conducted, namely the assumption of bromo complexes possessing the backbone of the chloro ones (Fig. 2, **C**). The above preference seems to be energetic in origin, since the $\mu$-Br coordination provides additional stabilization of both FMOs of about 2.3 eV. Furthermore, the bond energies in the two cases, i.e. the 'real' $\mu$-Br and the 'imaginary' $\mu$-S, vary considerably, except for the Cu–Br bond which is almost invariant to this structural alteration. The Cu–S bond is stabilized in the 'real' structure by *c.* 35% while a varying stabilization reaching even 72% relative to the $\mu$-S model is observed in the Cu–P bonds of the $\mu$-Br compounds. This point is of interest in view of the general observation of lower quantum yields for the bromine compounds relative to the corresponding chlorine ones.

Despite the support to the existing experimental evidence, the present computational study is far from complete and further ones are needed to confirm the above arguments, especially in the case of iodo compounds, while the phosphine electronic effect consideration is a goal of our following studies [34].

## Supplementary material

Lists of observed and calculated structure factors, positional and anisotropic thermal parameters of the H atoms and the positional and equivalent thermal parameters of the phenyl-carbon atoms are available from the authors on request. Lists of iteratively obtained $H_{ii}$ for S and C atoms of the thione molecules are also available.

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