Synthesis and photochemical study of Cu(I) complexes with tri-*p*-tolylphosphine and heterocyclic thiones. The crystal structure of $[CuCl(pymtH)(p\text{-}CH_3C_6H_4)_3P]_2$

P. Karagiannidis*, S. K. Hadjikakou, P. Aslanidis and A. Hountas**
University of Thessaloniki, Faculty of Chemistry, General and Inorganic Chemistry Department, P.O. Box 135, GR-540 06 Salonica (Greece)

(Received March 21, 1990; revised July 10, 1990)

Abstract

Reactions of $[Cu(tptp)X]_4$ (tptp = tri-*p*-tolyl-phosphine, X = Cl, Br or I) 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 $[Cu(tptp)(L)X]_2$. The complexes have been characterized by elemental analyses, IR, UV–Vis and ^1H NMR spectroscopy. The photochemical behaviour of these complexes in chloroform solutions has been investigated. Irradiation causes the release of the phosphine and the formation of dinuclear compounds containing a Cu_2S_2 core. The crystal structure of $[Cu(tptp)(pymtH)Cl]_2$ has been determined by single-crystal X-ray diffraction methods. The red crystals are triclinic, space group $P\bar{1}$ with $a = 19.512(2)$, $b = 10.388(3)$, $c = 14.474(2)$ Å, $\alpha = 99.00(2)$, $\beta = 73.28(1)$, $\gamma = 116.22(2)°$, $D_{calc} = 1.394$ M m^{-3}, $V = 1228.2(4)$ Å^3 and $Z = 1$. The molecule contains a planar Cu_2S_2 moiety with Cu–S bond lengths of 2.356(1) and 2.470(1) Å. The Cu–P and Cu–Cl distances are 2.227(1) and 2.300(1) Å, respectively. The Cu···Cu separation is 3.316(0) Å.

Introduction

Copper(I) complexes continuously attract considerable interest because of the metal–metal interaction in systems with d^{10} electronic configuration [1–3]. Along this line a vast amount of dimeric adducts with heterocyclic thione as ligands have been structurally characterized [4–8].

In a recent communication we have described a series of mixed-ligand complexes $[Cu(PPh_3)(L)X]_2$, where L represents one of the heterocyclic thiones py2SH, py4SH and pymtH [9]. These complexes have been found to be dimeric with the thione ligand bridging two metal atoms. The photochemical behaviour of these complexes has been studied [10].

In order to investigate the experimental conditions employed in synthetic reactions and the possible transformation of the complexes following the elimination of phosphine upon photolysis we report on the synthesis and characterization (physical properties and photochemical behaviour) of a new series of complexes of the general formula $[Cu(tptp)(L)X]_2$.

Experimental

Materials and instruments

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

The IR spectra 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. NMR spectra were recorded on a Brucker AW 80 spectrometer. Magnetic susceptibility measurements were carried out by the Faraday technique at several magnetic field strengths, using $Hg[Co(SCN)]_4$ as the calibrant. Conductivity measurements were performed with a Wheatstone bridge Model RC 216 B2 using 10^{-3} M chloroform solutions. Melting points were determined with a Büchi apparatus and are uncorrected. Elemental analyses for C, N and H

---

*Author to whom correspondence should be addressed.
**Present address: X-ray Laboratory, NCR 'Democritos', Athens, Greece.

were carried out with a Perkin-Elmer 280 elemental analyzer.

Quantum yields were measured in 1 cm quartz cells using a high pressure HBO 200W/4 Osram lamp, a 2 cm water filter and interference of a monochromator manufactured by Applied Photophysics. For the photolyses a Hg lamp manufactured by Sylvania was used. All the photochemical work was carried out in the dark.

Preparation of the complexes

$[Cu(tptp)X]_4$ (X = Cl, Br or I) was prepared by heating equimolar quantities of CuX and tptp at 50–70 °C in acetonitrile, for about 30 min. Complexes of the formula $[Cu(tptp)(L)X]_2$ were prepared according to the following general procedure. A solution of 0.4 mmol of the appropriate thione in 20 ml of methanol was added to a solution of 0.1 mmol of $[Cu(tptp)X]_4$ in 20 ml acetonitrile and the resulting solution was moderately heated. Refluxing conditions were necessary only in the case of the chloride complexes. The solution was 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.

Collection and reduction of intensity data

Single crystals of $[Cu(tptp)(pymtH)Cl]_2$ suitable for the subsequent crystal structure analysis were obtained by slow evaporation of a acetonitrile/methanol solution of the complex.

Complete crystal data and parameters for data collection are reported in Table 1. Unit cell dimensions were derived from a least-squares refinement of the setting angles of 15 automatically centered reflections in the range $50° < 2\theta < 52°$ on a Syntex $P2_1$ diffractometer with Ni-filtered Cu Kα radiation. The intensities of three standards monitored after 67 reflections were stable with a scatter of less than 3% from their respective means. Lp and absorption corrections were applied. The atomic scattering factors were taken from the International Tables for X-ray Crystallography [11]. The structure was solved by direct methods using SHELX86 [12], and was refined with SHELX76 [13] in the $P\bar{1}$ space group by full-matrix least-squares in which $\Sigma w \Delta^2$ was minimized. Attempts to refine it in $P1$ led to negative Us. H positions were located from a difference Fourier map, except for those of the methyl groups which were calculated as riding on carbons at 1.08 Å; non-H atoms anisotropic, H atoms isotropic. Two reflections showing poor agreement were given zero weight during final refinement cycles. The final atomic parameters and the anisotropic thermal parameters of the non-H atoms are given in Tables 2 and 3, bond lengths and angles in Table 4.

TABLE 1. Summary of crystal and intensity collection data

Formula	$Cu_2Cl_2(SN_2C_4H_4)_2(PC_{21}H_{21})_2$
Formula weight	1031
a (Å)	9.512(2)
b (Å)	10.388(3)
c (Å)	14.474(2)
α (°)	99.00(2)
β (°)	73.28(1)
λ (°)	116.22(2)
V (Å^3)	1228.2(4)
Z	1
D_{calc} (Mg m^{-3})	1.394
D_{meas} (Mg m^{-3})	1.39
Crystal dimensions (mm)	$0.13 \times 0.25 \times 0.33$
Space group	$P\bar{1}$
Radiation	Cu Kα
μ (cm^{-1})	36.47
Transmission factors	0.4272–0.6570
Scan speed (°/min)	3.0–20.0
Scan range (°)	1.65 plus α_1–α_2
Background counting (s)	0.7 of scan time
2θ limit (°)	124.0
Data collected	4390
Data unique	3861
R_{int}	0.0099
Data used	3599 with $F_o \geqslant 4.0\sigma(F_o)$
Range of hkl	$-10 \rightarrow 0$, $-10 \rightarrow 11$, $-16 \rightarrow 15$
Weighting scheme	$1/w = \sigma^2(F_o) + 0.0001\|F_o\|^2$
$F(000)$	530
No. refined parameters	362
$\|\Delta/\sigma\|_{max}$	0.183
$(\Delta p)_{max}$ (e Å^{-3})	0.265
$(\Delta p)_{min}$ (e Å^{-3})	−0.397
S[a]	2.26
R (obs.)[b]	0.0289
R (all data)[b]	0.0315
R_w (obs.)[c]	0.0394
R_w (all data)[c]	0.0402

[a] $S = [\Sigma w(\Delta F)^2/(N-P)]^{1/2}$, N = no. of observed reflections, P = no. of parameters. [b] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [c] $R_w = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$.

Results and discussion

Recently we have been working on a series of mixed Cu(I) complexes with heterocyclic thiones and phosphines as ligands [9, 14–16]. In the course of our studies we observed a darkening of their initially yellow coloured chloroform solutions challenging us to investigate the photochemistry of a series of such complexes.

All the prepared complexes are microcrystalline solids soluble in chloroform, acetonitrile, ethanol, methanol and acetone. Their elemental analyses confirm their stoichiometry and their physical properties are in accordance with the proposed structures. Room temperature magnetic measurements on sev-

TABLE 2. Positional and equivalent thermal parameters ($\times 10^4$) of the non-H atoms with e.s.d.s in parentheses

Atom	x	y	z	U^a
Cu	6966.5(4)	901.9(4)	4542.0(2)	504
P	8025.6(6)	1381.7(5)	2982.5(3)	357
Cl	8777.4(7)	1183.8(6)	5404.4(4)	543
S	4950.1(6)	1657.2(6)	5433.9(4)	444
C(1)	4696(3)	2596(2)	4679(2)	448
N(1)	5919(2)	3777(2)	4255(2)	576
C(2)	5597(4)	4495(3)	3724(2)	739
C(3)	4096(4)	4123(3)	3595(2)	904
C(4)	2887(4)	2920(3)	4008(2)	805
N(2)	3206(2)	2170(2)	4527(1)	551
C(11)	11038(3)	3145(2)	1817(2)	469
C(12)	12385(3)	4428(3)	1588(2)	554
C(13)	12611(3)	5618(2)	2200(2)	571
C(14)	11433(3)	5499(2)	3046(2)	665
C(15)	10076(3)	4228(2)	3279(2)	514
C(16)	9858(2)	3024(2)	2663(1)	390
C(17)	14117(4)	7004(3)	1964(3)	886
C(21)	8413(3)	−598(2)	1432(2)	491
C(22)	8754(3)	−1763(3)	1041(2)	554
C(23)	9284(3)	−2419(2)	1537(2)	463
C(24)	9502(3)	−1854(2)	2445(2)	488
C(25)	9162(3)	−696(2)	2846(1)	430
C(26)	8592(2)	−55(2)	2352(1)	345
C(27)	9608(4)	−3713(3)	1108(2)	793
C(31)	7271(3)	2216(3)	1466(2)	499
C(32)	6215(3)	2127(3)	957(2)	596
C(33)	4582(3)	1286(2)	1243(2)	523
C(34)	4030(3)	562(3)	2087(2)	506
C(35)	5081(3)	642(2)	2609(2)	445
C(36)	6725(2)	1444(2)	2297(1)	377
C(37)	3454(3)	1126(3)	642(2)	783

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

eral species confirm that the central metal ion is diamagnetic Cu(I). Their conductivity measurements reveal, as expected, a non-electrolytic nature.

Spectroscopy

The UV–Vis spectra of the complexes are dominated by two main absorptions in the regions 250–260 and 280–310 nm. The first band is ascribed to the intraligand transitions of the phosphine ligand, since the spectrum of the free phosphine consists of two bands at 245 and 260 nm having log ϵ values (*c.* 4.1) similar to those observed in the complexes, and it is well-known [17] that arylphosphines do not shift their intraligand bands upon coordination to Cu(I). The second band expresses a small red shift (10–20 nm) with respect to the corresponding one in the spectra of the free thiones. Therefore, this band, which is accompanied by a third one in the region 350–380 nm in the case of conjugated heterocyclic thiones should be ascribed to the intraligand transitions of the thione ligand [18]. No shoulders are detected in the above-mentioned bands, therefore it cannot be unambiguously stated whether they are accompanied by MLCT transitions. In order to reveal any CT character of these bands, the electronic spectra were recorded also in toluene, tetrahydrofuran and acetonitrile. The thione originating absorption bands expressed a small blue shift (no more than 10 nm) on going to more polar solvents.

Note should be made at this point that in the present study we are facing the conflicting effects of a coordinated phosphine molecule and halogen atom, which are known to cause shift of the MLCT bands to lower [19] and higher [20] wavelengths, respectively. In view of this fact and of our observation we may conclude that the intraligand thione bands possess partial CT character.

Infrared spectra in the region 4000–250 cm^{-1} provide information concerning the coordination mode of the ligands. Solid state infrared spectra exhibit the dominance of the thione form of the ligands investigated deduced by the presence of ν(NH) bands at 3200–3130 cm^{-1} [21–23], the absence of any evidence for ν(SH) bands in the 2500–2600 cm^{-1} [24, 25] region and the production of characteristic 'thioamide bands' [24] as well as the ν(Cu–S) bands at 370–340 cm^{-1} [26].

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 $\delta \sim 11$–14 ppm attributed to the NH protons, thus confirming the prevalence of the thione tautomer in the complexes.

Photolysis

Irradiation of copper(I) complexes at $\lambda_{exit} = 270$–310 nm in chloroform solution at room temperature causes the decomposition of the complexes within minutes, without the evolution of new bands. A relevant representation of the spectral changes for $[Cu(bzimtH)(tptp)I]_2$ during irradiation is depicted in Fig. 1. The maximum of the band in the region 270–310 nm was selected in all cases as the irradiation wavelength in the subsequent studies for the photodissociations and the quantum yield determinations. The decomposition of the complexes is not at all unexpected on the grounds of the lability of the tptp ligand in solution [27, 28] and in view of our results it could be summarized in the following equation

$$[Cu(tptp)(L)X]_2 \xrightarrow{h\nu} [Cu(L)X]_2 + 2\ tptp$$

In every case solid products were deposited and their constitution was verified by means of elemental analyses and by their physical and spectral properties.

The quantum yields at room temperature in each case have been determined from the variation of

TABLE 3. Anisotropic thermal parameters ($\times 10^3$) of the non-H atoms with e.s.d.s in parentheses

Atom	$U11$	$U22$	$U33$	$U12$	$U13$	$U23$
Cu	50.4(2)	66.4(2)	34.5(2)	31.1(2)	−8.9(2)	6.1(1)
P	34.9(3)	40.5(3)	31.7(2)	16.1(2)	−10.1(2)	1.9(2)
Cl	51.6(3)	61.3(3)	50.0(3)	27.5(3)	−23.6(2)	−4.0(2)
S	45.4(3)	48.8(3)	39.0(3)	24.8(2)	−10.0(2)	2.6(2)
C(1)	46.0(9)	47.5(9)	40.9(9)	27.5(7)	−7.2(3)	−0.7(7)
N(1)	53.5(9)	53.2(9)	66.1(9)	21.5(7)	−5.8(8)	16.8(8)
C(2)	82(1)	63(1)	77(1)	29.9(9)	−7(1)	25.0(10)
C(3)	96(1)	85(1)	90(1)	49(1)	−28(1)	28(1)
C(4)	74(1)	86(1)	82(1)	42.0(9)	−29(1)	14(1)
N(2)	49.1(9)	58.7(9)	57.5(9)	25.2(7)	−15.8(7)	9.5(8)
C(11)	47.1(9)	46.0(9)	47.6(9)	9.8(8)	−9.3(8)	−5.5(8)
C(12)	51(1)	59(1)	57(1)	6.3(9)	−8.2(9)	7.9(9)
C(13)	60(1)	42.8(9)	69(1)	5.2(8)	−29.3(9)	12.2(9)
C(14)	78(1)	39.8(9)	81(1)	22.5(9)	−43.1(9)	−15.7(9)
C(15)	53(1)	50.2(9)	50.7(9)	23.5(8)	−17.4(8)	−7.9(8)
C(16)	38.0(8)	40.1(8)	38.9(8)	16.3(7)	−15.5(7)	−1.0(7)
C(17)	100(1)	54(1)	112(1)	−16(1)	−41(1)	18(1)
C(21)	55.4(9)	50.9(9)	41.1(9)	25.2(8)	−22.7(8)	−2.8(8)
C(22)	64(1)	58(1)	43.8(9)	30.0(8)	−23.5(8)	−13.9(8)
C(23)	44.1(9)	43.1(9)	51.8(9)	17.5(8)	−9.4(8)	−1.3(8)
C(24)	47.3(9)	51.0(9)	48.1(9)	25.3(8)	−11.9(8)	6.1(8)
C(25)	41.8(9)	51.4(9)	35.8(8)	21.6(7)	−12.4(7)	1.7(7)
C(26)	30.4(8)	38.2(8)	34.8(8)	11.8(7)	−9.0(7)	2.3(7)
C(27)	97(1)	64(1)	77(1)	49.7(9)	−21(1)	−11.1(9)
C(31)	38.2(9)	61(1)	50.8(9)	13.7(8)	−10.7(8)	19.9(8)
C(32)	56(1)	71(1)	51.6(9)	23.9(9)	−15.8(8)	20.9(9)
C(33)	48.7(9)	57.3(9)	50.9(9)	29.6(8)	−21.2(8)	−5.1(8)
C(34)	35.4(9)	34(1)	52.9(9)	17.2(8)	−13.1(8)	2.8(8)
C(35)	38.6(9)	53.0(9)	42.0(9)	17.2(8)	−9.7(8)	5.5(8)
C(36)	37.6(3)	39.3(8)	36.1(8)	18.1(7)	−11.0(7)	−0.1(7)
C(37)	63(1)	99(1)	73(1)	43.0(9)	−34.5(9)	2(1)

the concentration with irradiation time vs. the I_λ of the lamp which was calculated with respect to the standard potassium ferroxalate system. The observed quantum yields are presented in Table 5.

Description of the crystal structure

The atomic labeling of the complex is depicted schematically in Fig. 2 and a stereoview of the molecule is presented in Fig. 3. Bond distances and angles are reported in Table 4. The complex exists as dimer with a crystallographically imposed centre of symmetry. The pyrimidine-2-thione molecules are monodentate with the sulfur atoms as bridging coordinating groups. Each copper atom possesses a distorted tetrahedral geometry. The copper atom is surrounded by a P atom from tri-*p*-tolyl-phosphine, a chlorine atom and two non-equivalent, double bridging sulfur atoms.

The reported Cu–S distances in the complex are comparable to those in other binuclear Cu(I) complexes with double bridging sulfur atoms, e.g. $[CuI(py2SH)]_2$ (2.328(1) and 2.577(2) Å), $[Cu(py2SH)_3]Cl_2$ (2.298(3) and 2.538(4) Å) and $[Cu(py2SH)_3]Br_2$ (2.774(2) and 2.534(3) Å) [4]. In the structure of $[Cu(PPh_3)(pmtH)Br]_2$ [9] the analogous bond lengths are 2.383(5) and 2.392(2) Å.

The two individual Cu–P distances are both 2.227(1) Å and are comparable to those found in other four coordinate copper(I)–phosphine complexes [2]. As there are no other forces reasoning the strain resulting from the P atoms of the phosphine groups, the large value of the Cu–S(1) bond length probably reflects the substitution of the Br atom by the more electronegative chlorine atom.

The Cu–Cl bond distance of 2.300(1) Å is shorter than that found for tetrahedral Cu(1) (2.340 Å) [29] but is longer than the corresponding one in monomeric complexes with trigonal coordination around the Cu atom, probably because of the intramolecular Cl···H bridging bonds (N(2)–HN(2) = 0.92(1) Å, HN(2)···Cl = 2.30(1) Å, N(2)···Cl = 3.146(2) Å, N(2)–HN(2)···Cl = 152.3(9)°).

The bridging sulfur atoms and the two copper atoms form a parallelogram with two short and two

TABLE 4. Interatomic distances (Å) and angles (°) for $[Cu(pymtH)(p\text{-}MePh_3P)Cl]_2$ with e.s.d.s given in parentheses

Distances			
Cu–P	2.227(1)	C13–C17	1.514(3)
Cu–Cl	2.300(1)	C14–C15	1.380(3)
Cu–S	2.356(1)	C15–C16	1.389(5)
P–C16	1.822(2)	C21–C22	1.385(4)
P–C26	1.831(2)	C21–C26	1.390(3)
P–C36	1.821(3)	C22–C23	1.377(4)
S–C1	1.703(3)	C23–C24	1.388(3)
N1–C1	1.341(2)	C23–C27	1.511(4)
N2–C1	1.359(3)	C24–C25	1.380(4)
N1–C2	1.325(5)	C25–C26	1.393(4)
C2–C3	1.366(5)	C31–C32	1.372(4)
C3–C4	1.345(4)	C31–C36	1.391(3)
N2–C4	1.337(5)	C32–C33	1.375(3)
C11–C12	1.383(3)	C33–C34	1.380(3)
C11–C16	1.381(3)	C33–C37	1.507(5)
C12–C13	1.375(3)	C34–C35	1.386(4)
C13–C14	1.381(3)	C55–C36	1.379(3)
Angles			
P–Cu–Cl	115.4(0)	C14–C15–C16	120.7(2)
P–Cu–S	119.5(0)	P–C16–C11	122.9(2)
Cl–Cu–S	112.5(0)	P–C16–C15	119.2(1)
Cu–P–C16	117.6(1)	C11–C16–C15	117.8(2)
Cu–P–C26	109.1(1)	C22–C21–C26	120.4(3)
C16–P–C26	104.5(1)	C21–C22–C23	122.0(2)
Cu–P–C36	117.7(1)	C22–C23–C24	117.7(2)
C16–P–C36	103.4(1)	C22–C23–C27	121.2(2)
C26–P–C36	102.8(1)	C24–C23–C27	121.1(3)
Cu–S–C1	107.1(1)	C23–C24–C25	121.1(3)
S–C1–N1	121.5(2)	C24–C25–C26	121.1(2)
S–C1–N2	119.3(1)	P–C26–C21	124.3(2)
N1–C1–N2	119.1(2)	P–C26–C25	117.8(1)
C1–N1–C2	117.7(2)	C21–C26–C25	117.8(2)
N1–C2–C3	124.3(2)	C32–C31–C36	120.9(2)
C2–C3–C4	117.3(4)	C31–C32–C33	122.0(2)
C4–C4–N2	118.9(3)	C32–C33–C34	117.2(3)
C1–N2–C4	122.6(2)	C32–C33–C37	121.3(2)
C12–C11–C16	121.0(2)	C34–C33–C37	121.5(2)
C11–C12–C13	121.3(2)	C33–C34–C35	121.4(2)
C12–C13–C14	117.8(2)	C34–C35–C36	120.9(2)
C12–C13–C17	121.1(2)	P–C36–C31	124.7(2)
C14–C13–C17	121.0(2)	P–C36–C35	117.8(2)
C13–C14–C15	121.4(2)	C31–C36–C35	117.4(2)

longer Cu–S bonds, 2.356(1) and 2.470(1) Å; respectively. The Cu_2S_2 core is similar to that of $[Cu(py2SH)_3]_2X_2$, X = Cl, Br [4]. Of interest also are the short Cu···Cu and S···S distances, 3.316(1) and 3.508(1) Å, respectively. The copper–copper distance is comparable to the analogous one in $[Cu(PPh_3)(py2SH)Br]_2$ (3.420(3) Å) [9] and $[Cu(purinium\text{-}6\text{-}thione)Cl_2]_2$ (3.456(3) Å) [30].

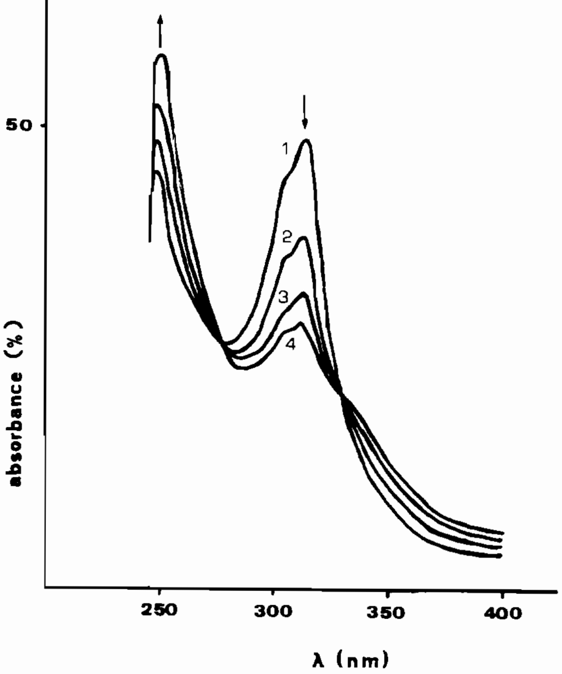

Fig. 1. UV absorption spectrum of a 2×10^{-5} M $CHCl_3$ solution containing $[Cu(bzimtH)(tptp)I]_2$ after irradiation at room temperature for (1) 0, (2) 3, (3) 6 and (4) 9 min.

The S–Cu–S and Cu–S–Cu angles (93.24(2) and 86.72(3)°) deviate significantly from the ideal values (109.5 and 70.5°) for a symmetric dimer, reflecting the distortions induced by the hydrogen contacts N–H···Cl. However, these angles are close to the predicted geometry assumed by Summerville and Hoffmann [31] for $Y_2MX_2MY_2$ dimers (S–Cu–S = 95–100°, Cu–S–Cu = 85–80° and Cu···Cu = 3.0–3.2 Å). According to Mehrotra and Hoffmann, the factors which govern Cu_2S_2 core formation are a combination of bonding and steric requiments of the bridging ligand and soft attractive Cu···Cu coupling [32]. Raper and co-workers [7] observed in a series of centro-symmetric dimers with related ligands that opening up of the bridging Cu–S–Cu angle is accompanied by a shortening of the S···S separation and an increase of the metal–metal one, together with an elongation of the two Cu–S distances.

The Cu–P–C(16) and Cu–P–C(36) angles (117.6 and 117.7°) deviate significantly form the ideal tetrahedral value, but the Cu–P–C(26) angle (104.5°) is less than the tetrahedral value. The Cu–S–C angle (107.1°) is not far from the tetrahedral value and is in the range previously observed for coordinated py2SH molecules. The Cl–Cu–P angle of 115.4(0)° is comparable with the analogous angle 114.8(1)° observed in the pyridine-2-thione complex [9].

Within the tri-*p*-tolylphosphine and the pyrimidine-2-thione molecules the distances and angles are

TABLE 5. Irradiation wavelengths and calculated quantum yields of the studied complexes

No.	Complex	λ_{exit}	log ϵ	C (mol l^{-1})[a]	Φ
1	$[Cu(tptp)(py2SH)Cl]_2$	295	4.3	3.89	0.143
2	$[Cu(tptp)(py2SH)Br]_2$	293	4.2	3.34	0.081
3	$[Cu(tptp)(py2SH)I]_2$	295	4.1	4.71	0.144
4	$[Cu(tptp)(pymtH)Cl]_2$	293	4.4	2.89	0.019
5	$[Cu(tptp)(pymtH)Br]_2$	300	4.0	4.56	0.017
6	$[Cu(tptp)(pymtH)I]_2$	290	3.8	3.09	0.048
7	$[Cu(tptp)(tztdH)Cl]_2$	300	4.0	5.39	0.081
8	$[Cu(tptp)(tztdH)Br]_2$	298	3.9	5.57	0.064
9	$[Cu(tptp)(tztdH)I]_2$	290	4.0	3.32	0.053
10	$[Cu(tptp)(meimtH)Cl]_2$	265	3.5	3.79	0.147
11	$[Cu(tptp)(meimtH)Br]_2$	268	4.0	1.79	0.085
12	$[Cu(tptp)(meimtH)I]_2$	270	4.1	0.78	0.085
13	$[Cu(tptp)(bzimtH)Cl]_2$	310	4.0	1.79	0.497
14	$[Cu(tptp)(bzimtH)Br]_2$	310	3.8	6.03	0.627
15	$[Cu(tptp)(bzimtH)I]_2$	310	3.9	6.60	0.877
16	$[Cu(tptp)(qntH)Cl]_2$	295	4.1	5.12	0.020
17	$[Cu(tptp)(qntH)Br]_2$	293	4.1	5.52	0.024
18	$[Cu(tptp)(qntH)I]_2$	290	4.1	3.32	0.029

[a] Concentration values multiplied by 10^5.

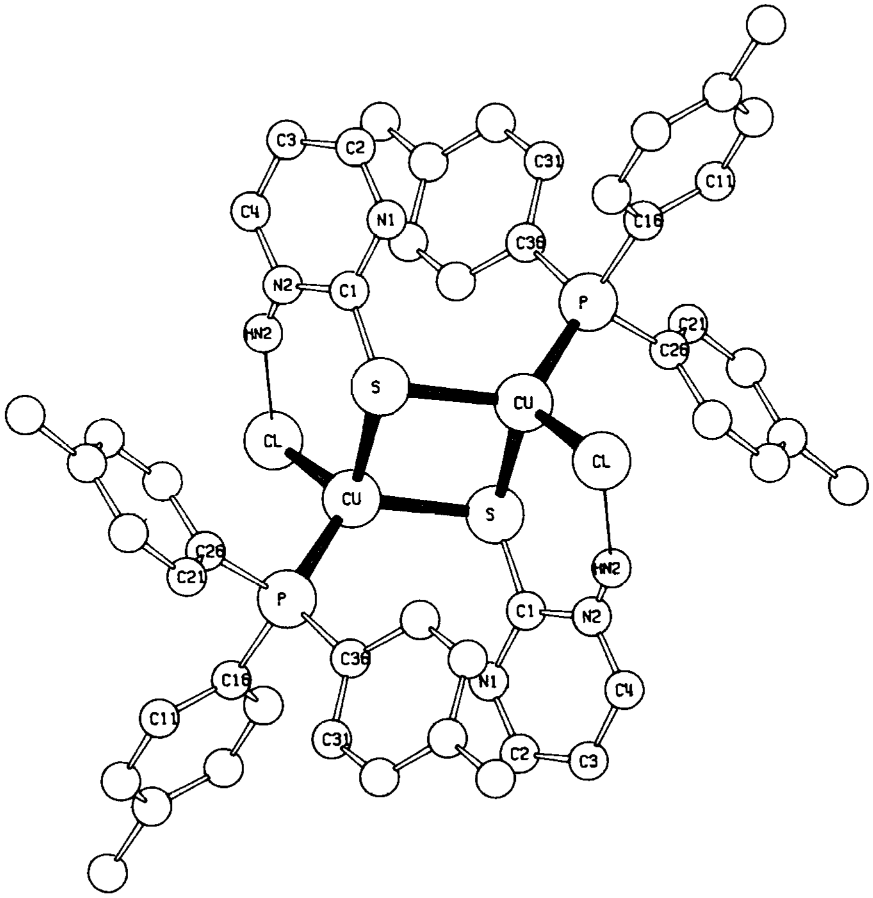

Fig. 2. A view of the complex. Thin lines denote N–H···Cl hydrogen bonds.

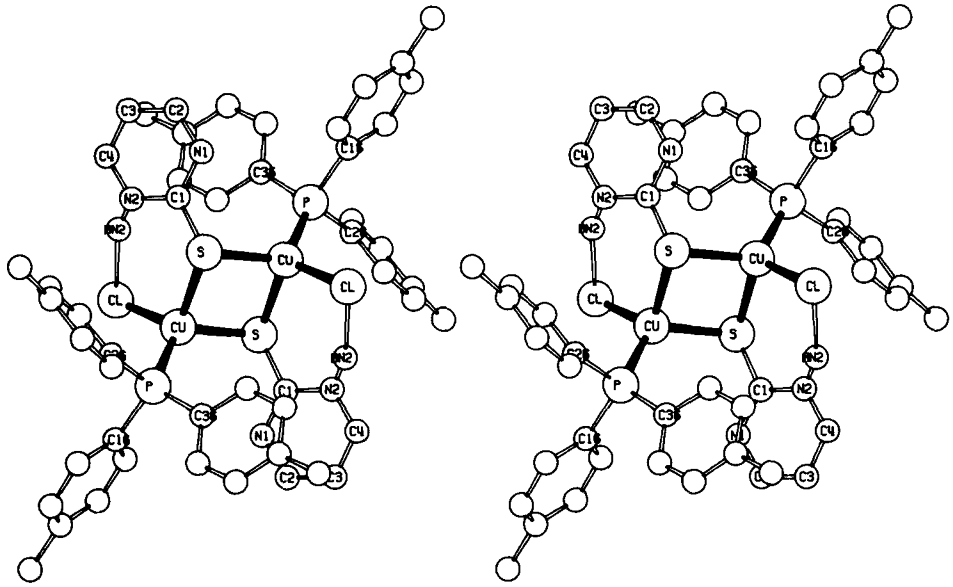

Fig. 3. A stereoview of the complex.

consistent with those commonly found in other complexes containing such molecules as ligands.

Supplementary material

A table representing the elemental analyses and a few relevant physical properties of the complexes, lists of observed and calculated structure factors, of positional and anisotropic thermal parameters of the H atoms and of the positional and equivalent thermal parameters of the phenyl-carbon atoms are available from the authors on request.

References

1 I. G. Dance, P. J. Guerney, A. D. Rae and M. L. Scudder, *Inorg. Chem., 22* (1983) 2883.
2 M. R. Churchill and K. L. Kalra, *Inorg. Chem., 13* (1974) 1065.
3 I. G. Dance, M. L. Scudder and L. J. Fitzpatrick, *Inorg. Chem., 24* (1985) 2547.
4 G. A. Stergioudis, S. C. Kokkou, P. J. Rentzeperis and P. Karagiannidis, *Acta Crystallogr., Sect. C, 43* (1987) 1685.
5 E. C. Constable and P. R. Raithby, *J. Chem. Soc., Dalton Trans.,* (1987) 2281.
6 M. R. Caira and L. R. Nassimbeni, *Acta Crystallogr., Sect. B, 31* (1975) 1339.
7 J. R. Creighton, D. J. Gardiner, A. C. Gorvin, C. Gutteridge, A. R. W. Jackson, E. S. Raper and P. M. A. Sherwood, *Inorg. Chim. Acta, 103* (1985) 195.
8 D. Mentzafos, A. Terzis, P. Karagiannidis and P. Aslanidis, *Acta Crystallogr., Sect. C, 45* (1987) 54.
9 P. Karagiannidis, P. Aslanidis, D. P. Kessissoglou, B. Krebs and M. Dartmann, *Inorg. Chim. Acta, 156* (1989) 47.
10 P. Aslanides, P. Karagiannides and S. Hadjikakou, *Abstr., 1st Chemistry Conf, Cyprus, Greece, Sept. 23–27, 1988,* Ass. of Greek Chemists, Nicosia, Cyprus, p. 90.
11 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1974.
12 G. M. Sheldrick, *SHELX 76,* program for crystal structure determination, University of Cambridge, U.K., 1976.
13 G. M. Sheldrick, in G. M. Sheldrick, C. Kruger and R. Goddart (eds.), *Crystallographic Computing,* Oxford University Press, London, 1985, pp. 175–189.
14 P. Karagiannidis, P. Aslanidis, S. Papastefanou, D. Mentzafos, A. Hountas and A. Terzis, *Inorg. Chim. Acta, 156* (1989) 277.
15 C. Lecomte, S. Skoulika, P. Aslanidis, P. Karagiannidis and S. Papastefanou, *Polyhedron, 8* (1989) 1103.
16 P. Karagiannidis, P. Aslanidis, S. Papastefanou, D. Mentzafos, A. Hountas and A. Terzis, *Polyhedron, 9* (1990) 981.
17 S. W. Orchard and C. Kutal, *Inorg. Chem., 21* (1982) 538.
18 L. Casella, *Inorg. Chem., 23* (1984) 2781.
19 M. T. Buckner and D. R. McMillin, *J. Chem. Soc., Chem. Commun.,* (1978) 759.
20 S. Kitagawa, M. Munakata and A. Higashie, *Inorg. Chim. Acta, 59* (1982) 219.

21 A. W. McLellan and G. A. Melson, *J. Chem. Soc. A,* (1967) 137.

22 P. P. Singh and R. Rivest, *Can. J. Chem., 46* (1968) 2361.

23 B. Singh, M. M. Rukhaivar and R. J. Sinha, *J. Inorg. Nucl. Chem., 39* (1977) 29.

24 C. N. R. Rao and P. Vankataraghavan, *Spectrochim. Acta, 18* (1962) 541.

25 E. S. Raper and J. L. Brooks, *J. Inorg. Nucl. Chem., 39* (1977) 2163.

26 L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* Wiley, New York, 1966.

27 E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc., 92* (1970) 4114.

28 D. J. Fife, W. M. Moore and K. W. Morse, *Inorg. Chem., 23* (1984) 1545.

29 L. Pauling, in *The Nature of the Chemical Bond,* Cornel University Press, Ithaca, 3rd edn., 1960.

30 A. C. Shoemaker, P. Singh and D. J. Hodgson, *Acta Crystallogr., Sect. B, 32* (1976) 979.

31 R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc., 98* (1976) 7240.

32 P. K. Mehrotra and R. Hoffmann, *Inorg. Chem., 17* (1978) 2187.